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KRAFT EFFLUENT COLOR CHARACTERIZATION BEFORE AND AFTER STOICHIOMETRIC LIME TREATMENT

John W. Swanson, et al

Institute of Paper Chemistry
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Kraft Effluent Color Characterization Before and After Stoichiometric Lime Treatment

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The "weight average" molecular weights ($\bar{M}_w$) of the untreated acid-insoluble fractions varied from < 400 to 30,000 and of the untreated acid-soluble, lime-treated acid-insoluble, and lime-treated acid-soluble fractions from < 400 to 5000.

The study shows that color bodies having an apparent $\bar{M}_w$ of < 400 are not removed by lime treatment and those having $\bar{M}_w$ of 5000 and above are completely removed. The intermediate range of $\bar{M}_w$ 400 to 5000 apparently undergoes partial removal.

Infrared spectroscopy data indicate that the acid-insoluble color bodies (high $\bar{M}_w$) contain a high proportion of conjugated carboxyl groups where conjugation with an aromatic ring is probable. The acid-soluble fractions (low $\bar{M}_w$) seem to contain non-conjugated carboxyl groups and may be associated with carbohydrate material. However, color bodies are found to be aromatic in nature (partially degraded lignin), possess a negative charge, and exist primarily as soluble sodium salts in aqueous solutions.

The color bodies which are not removed by lime treatment have low $\bar{M}_w$, high non-conjugated carboxyl groups, some lignin-like character, and seem to be associated with colorless carbon compounds.

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SECTION I

CONCLUSIONS

Conclusions are divided into two categories: Observations and Major Conclusions.

Observations

Eight series of composite unbleached kraft mill waste samples were shipped from Riceboro, Georgia to Appleton, Wisconsin. Analysis of these samples before and after shipment (lapse time 3-4 days) showed that no appreciable changes occurred in color, total solids, fixed solids (ash), and volatile content during shipment.

Visible spectra were recorded on a series of four dilutions of the untreated waste samples. The pH was adjusted to 7.6 in each case. The decrease in absorbance values with dilution was found to be linear, demonstrating that the Beer-Lambert law was being observed in the visible region. This suggests that a direct correlation between absorbance and concentration exists.

Freeze-drying of color bodies was carried out. No significant changes in color, absorbance, and total organic carbon (TOC) were noticed on samples before and after freeze-drying. However, freeze-dried color bodies from the lime-treated wastes showed an average decrease of 45 percent in their sedimentation coefficient values indicating a decrease in molecular weight or an increase in hydration of the sedimenting molecules. Upon redissolution of the freeze-dried color bodies, an opaque colorless sediment was noticed which had to be removed before sedimentation coefficient measurements were conducted. This sediment was found to be mainly silica and some starch. It is possible that loss of these materials from the colored solutions resulted in lower sedimentation coefficients.

The carbonate content of the color bodies was found to increase during processing, freeze-drying, and conditioning. This increase was found to be due to the absorption of carbon dioxide from the atmosphere. The freeze-dried color bodies were, therefore, conditioned to a constant weight in air before storage.

A concentrated solution of freeze-dried color bodies could be acidified to pH 1.0 to give acid-insoluble and acid-soluble components. The data indicated that the combined color recoveries of the acid-insoluble and acid-soluble components were 93 percent in the case of untreated waste and 81 percent in the case of lime-treated wastes. The corresponding TOC recoveries were 77 percent and 32 percent, respectively. Aqueous

alkaline solutions of these materials could be further fractionated into various molecular weight ranges on Bio-Gel columns.

Major Conclusions

1. The lime treatment process on an average removed about 86 percent color, 57 percent TOC, and 17 percent sugars, indicating that the remaining 43 percent TOC was responsible for only 14 percent of the original color. Most of this TOC is believed to be in the form of carbohydrate degradation products, resin acids, fatty acids, etc.

2. The data also indicate that the acid-insoluble components of mill wastes lost 94.3 percent color and 94 percent TOC, whereas acid-soluble components lost only 74.4 percent color and 43.4 percent TOC during the lime treatment.

3. Infrared spectroscopy shows that the acid-insoluble color bodies (high M_w) contain a high proportion of carbonyl groups (carboxyl, ketone, or both) conjugated with an aromatic ring, whereas the acid-soluble fractions (low M_w) seem to contain nonconjugated carboxyl groups, and seem to be associated with carbohydrate material.

4. The "weight average" molecular weights (M_w) of the untreated acid-insoluble fractions varied from < 400 to 30,000 and of the untreated acid-soluble, lime-treated acid-insoluble, and lime-treated acid-soluble fractions from < 400 to 5000.

5. Color bodies having an apparent M_w of < 400 are not removed by lime treatment and those having M_w of 5000 and above are completely removed. The intermediate range of M_w 400 to 5000 apparently undergoes partial removal.

6. Most of the color bodies are ligninlike in character and appear to consist of lignins which have been degraded to various degrees.

7. In aqueous media color bodies are soluble as salts (especially sodium salts). Decationization by cation exchange resin resulted in precipitation of color bodies.

8. Gel electrophoretic studies showed that all isolated color bodies are negatively charged. Except a few color bodies, all others showed mobilities higher than Indulin (alkali lignin), indicating a higher density of negative charge per molecule.

9. The color bodies which are not removed by lime treatment have low M_w, high nonconjugated carboxyl groups, some ligninlike character, and seem to be associated with colorless carbon compounds (carbohydrate material, rosin acids, etc.).

SECTION II

RECOMMENDATIONS

On the basis of this study, the following recommendations are made.

1. Because the absorption of radiation by color bodies varies with pH and time, the spectrophotometric studies must be performed at a constant pH as soon as possible after sampling.

2. As it is pH dependent, the color of two different wastes should be compared at the same pH.

3. Freeze-dried color bodies must be conditioned in air to a constant weight before storage to minimize weight fluctuations caused by carbon dioxide absorption.

4. Preliminary studies, based upon the observation that color bodies which are not removed by lime are of low molecular weights and contain high nonconjugated carboxyl groups, have shown that multivalent cations could be used with lime (before or after lime treatment) to achieve over 99 percent color removal. An extensive study on the use of such cations with lime is presently in progress at The Institute of Paper Chemistry.

5. Color bodies which are not removed by lime are also found to be associated with the carbohydrate material. In order to reduce the negative effect, if any, of the carbohydrates on the efficiency of lime treatment, the mill wastes should be passed through a bicoxidation stage before the addition of lime. It is proposed that such work be carried out first in the laboratory.

6. A study on the effect of various degrees of pulping on molecular weight of color bodies in mill effluents and their subsequent lime treatment should be conducted.

7. It would be useful to obtain additional UV- and IR-spectra of samples with considerably lower inorganic content. Tentative suggestions regarding possible differences in relative amounts of aromatic and aliphatic molecular units would be worthy of further investigation using nuclear magnetic resonance (NMR) spectroscopy.

SECTION III

INTRODUCTION

Recently, the pulp and paper industry has given major attention to the effect of mill effluents on receiving water color and to the development of means for reducing the discharge of colored organic material to such waters. Major sources of color from the pulp mill are the caustic extraction stage in bleaching, and the unbleached screening and decker filtrates. It is believed that the colored material originates from lignins and lignin derivatives which are washed out of the cooked pulp. Since lignin is highly resistant to microbiological degradation, the color passes through the biological treatment processes. The colored effluents make the receiving waters brownish in color and reduce the light penetration in water. This reduction in light intensity affects aquatic plants by reducing photosynthesis and thereby adversely affects the dissolved oxygen content of water.

The lime-treatment process developed by the National Council of The Pulp and Paper Industry for Air and Stream Improvement (NCASI) is reported to be capable of removing about 90 percent of the color from both bleaching and pulping effluents[1-5]. This process has gone through the pilot-plant stage and at present is being used by several mills.

Although the technology of lime treatment is well developed, conflicting results have been reported with respect to the underlying chemistry of the process. However, recent studies by Dence, et al.[6] have shown that the removal of colored material from spent caustic extraction liquor with lime is a chemical rather than a physical process and that color removal is dependent on (a) the presence of enolic and phenolic hydroxyl groups, and (b) on the molecular weight of solids contained in the liquor. No data on the molecular weight distribution were reported.

This report presents work done on the characterization of color bodies before and after lime treatment of the decker wastes from the Interstate Paper Corporation kraft linerboard mill at Riceboro, Georgia. The general objective of the project was the isolation of the colored components of the dilute kraft waste liquors before and after stoichiometric lime treatment and their subsequent characterization. It is generally known that such brown-colored materials are complex mixtures of more-or-less acidic polymers which are chemically sensitive. Such materials when isolated frequently tend to condense further into intractable, amorphous solids. Although the colored fractions, herein described, appeared to be reasonably stable one must assume that each separation may have been accompanied by minor chemical changes, at least.

The project approach was divided into three major categories:

1. Initial Characterization and Handling of Colored Wastes.
2. Isolation and Fractionation of Color Bodies.
3. Characterization of Color Bodies.

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SECTION IV

INITIAL CHARACTERIZATION AND HANDLING OF COLORED WASTES

Sampling and Handling

Twenty-four-hour composite samples of untreated decker waste (U-Series), lime-treated waste containing color bodies that are not removed by lime treatment (LT-Series), and returned waste containing supernatant from sludge holding ponds and returned to the treatment process (R-Series), were shipped by air from Riceboro, Georgia to Appleton, Wisconsin. The samples were shipped in five-gallon polyethylene jugs enclosed in specially designed wooden crates provided by The Institute of Paper Chemistry. The usual transit time was two to three days. Samples in transit longer than three days were discarded. Eight series of samples were received over a period of 15 months in this manner. The R-Series were used for purposes of comparison only.

Chemical Characterization

Upon receipt at the Institute, representative aliquots of the liquid wastes were chemically analyzed and the data are given in Tables 1, 2, and 3. A comparison of these data with that obtained before shipment from Riceboro, Georgia, indicated that no appreciable changes in color, total solids, fixed solids, and volatiles occurred during shipment of the samples from Riceboro to Appleton under the sampling and shipping conditions recommended by the Institute. Calculation from the data showed that on an average about 86 percent color and 57 percent total organic carbon are removed by the lime-treatment process under study.

Spectrophotometric Examination of Liquid Wastes

The ultraviolet and visible spectra of the waste samples of Series One and Two were found to be similar and representative of other series. The absorption characteristics of Series Two, discussed in the following sections, may be considered to apply to all samples.

The spectra were recorded with a Beckman Model DK-2 ratio recording spectrophotometer, at the original pH and pH 7.6. Distilled water was used as a reference for all of the samples. The following was observed.

Visible Spectra

a. All of the samples exhibited an increase in absorbance as the wavelength decreased (750-350 nm).

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TABLE 1

ANALYTICAL DATA ON KRAFT LINERBOARD UNTREATED DECKER WASTE WATER

Sample Designation	U1	U2	U3	U4	U5	U6	U7	U8	Range	Avg
Month of Sampling	Jan.	March	May	Sept.	Oct.	Dec.	Jan.	March		
pH	10.9	11.6	9.6	10.1	10.3	10.3	11.2	10.2	9.6-11.6	10.5
Color Units										
at original pH	905	--	--	1100	980	1100	2000	440	440-2000	1087
at pH 7.6	705	380	560	800	660	820	1200	300	300-1200	680
Sodium, mg/l	341	466	336	372	402	286	443	350	286-466	374.5
Calcium, mg/l	61	132	44	2.4	9.2	14	16	22	2.4-132	28.0
Organic Nitrogen, mg/l	--	--	1.7	2.4	2.8	--	--	--	1.7-2.8	2.3
Organic Carbon, mg/l	--	125	120	200	190	195	355	125	120-355	186
Total Solids, mg/l	1360	1526	1212	1540	1600	1340	2100	1450	1212-2100	1516
Fixed Solids (Ash), mg/l	920	1241	898	1070	1090	893	1320	1140	893-1320	1073
Volatiles, mg/l	440	285	314	470	510	447	780	310	310-780	443
Carbonate, mg/l	--	--	121	178.5	184	132.5	256	140.5	121-256	172

TABLE 2

ANALYTICAL DATA ON KRAFT LINERBOARD LIME-TREATED DECKER WASTE WATER

Sample Designation	LT1	LT2	LT3	LT4	LT5	LT6	LT7	LT8	Range	Avg
pH	12.1	12.3	12.1	12.2	12.2	12.2	12.5	12.2	12.1-12.5	12.2
Color Units										
at original pH	250	--	--	360	280	280	400	150	150-400	287
at pH 7.6	105	90	50	160	120	120	170	60	50-170	109
Sodium, mg/l	306	405	310	414	411	264	434	396	264-434	367.5
Calcium, mg/l	488	505	440	335	340	378	407	456	335-505	419
Organic Nitrogen, mg/l	--	--	3.6	3.0	2.1	--	--	--	2.1-3.6	2.9
Organic Carbon, mg/l	--	60	45	110	90	100	120	45	45-120	80
Total Solids, mg/l	2060	2239	1818	2080	1920	1790	2220	2210	1790-2239	2042
Fixed Solids (Ash), mg/l	1630	1827	1420	1580	1560	1380	1730	1740	1380-1827	1608
Volatiles, mg/l	430	412	398	500	360	410	490	470	398-500	434
Carbonate, mg/l	--	--	171	150	82.5	96.5	217.5	250	82.5-250	161.2

TABLE 3

ANALYTICAL DATA ON RETURNED WASTE WATER FROM LIME-ORGANIC SLUDGE HOLDING PONDS

Sample Designation	R1	R2	R4	R5	R7	R8	Range	Avg
pH	11.6	11.4	11.5	11.5	11.6	11.4	11.4-11.6	11.5
Color Units								
at original pH	855	--	520	860	860	900	520-900	779
at pH 7.6	660	580	320	480	500	520	320-660	501
Sodium, mg/l	--	500	368	417	520	578	368-578	475
Calcium, mg/l	62	34	0.8	2.0	4	<2	1-62	17
Organic Nitrogen, mg/l	--	--	1.5	1.6	--	--	1.5-1.6	1.6
Organic Carbon, mg/l	--	156	103	178	220	196	103-220	171
Total Solids, mg/l	1490	1577	1380	1640	1900	2040	13.80-2040	1671
Fixed Solids (Ash), mg/l	1060	1238	1090	1240	1470	1560	1060-1560	1276
Volatiles, mg/l	430	339	290	400	430	480	290-480	395
Carbonate, mg/l	--	--	255	292	344	390	255-390	320

b. None of the samples contained an absorption maximum in this region.
c. The untreated waste and the returned waste (sludge pond supernatant) gave comparable absorbance values.
d. The lime-treated waste exhibited lower absorption than the other two samples through this region.
e. After adjusting the waste samples at pH 7.6 a general decrease in absorbance was observed.

The visible spectra demonstrated that no single color is present in the waste samples, rather they are mixtures of different colors as characterized by the increase in absorption as the wavelength decreases. In addition, it was demonstrated that lime treatment decreases the amount of color-giving materials.

Ultraviolet Spectra

a. The samples exhibited increased absorbance as the wavelength decreased (350-230 nm).
b. The absorption patterns of untreated and returned wastes were quite similar. Returned wastes gave higher absorption values.
c. Lime-treated waste gave the lowest absorption values.

The ultraviolet spectra indicated that the mill wastes contain materials similar to those present in lignin and that the amount of these materials decreases by lime treatment.

The effects of dilution, pH, and lime on absorbance were also studied.

Effect of Dilution on Absorbance at pH 7.6

Visible spectra were recorded on a series of four dilutions of the untreated sample. The pH was adjusted to 7.6 in each case.

The decreases in absorbance values with dilution were found to be linear (Figure 1), demonstrating that the Beer-Lambert law was being observed in the visible region and suggests that a direct correlation between absorbance and concentration exists.

Effect of pH on Absorbance at Constant Dilution

The pH of the untreated sample was varied between 11.0 and 2.0 in six steps. The upper limit of 11.0 was set as this was the pH of most of the original waste water samples. The lower limit of 2.0 was set because below this pH most of the color bodies became insoluble (slight precipitation was noticed at all pH on the acid side). The points between pH 2.0 and 11.0 were chosen at random.

The absorbance data illustrated that the lowest pH value gave the lowest absorbance value and that the absorbing materials (color producing) are

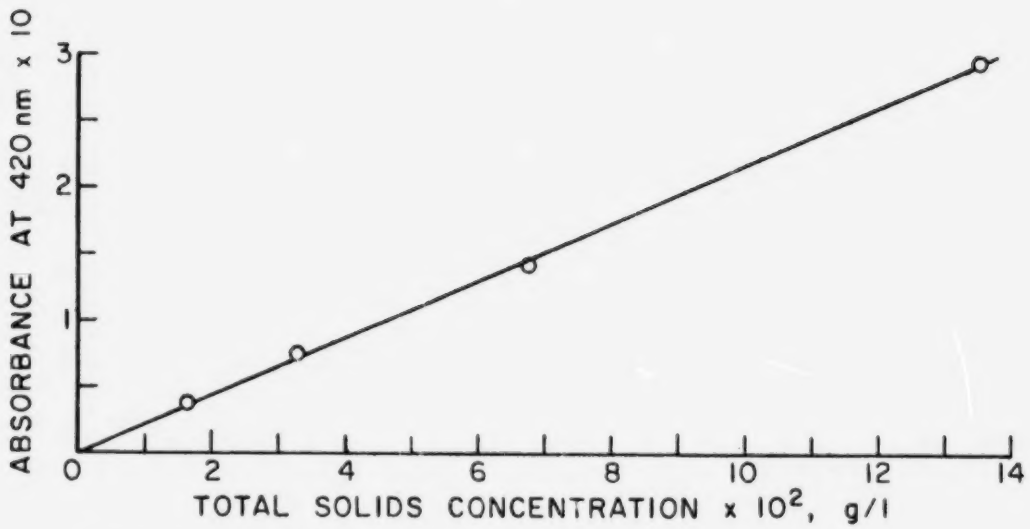

Figure 1. Correlation of Solids Concentration with Absorbance (at 420 nm) of Untreated Waste

pH sensitive (Figure 2). As the pH increased, the absorbance values increased until a pH of approximately 5 was obtained. Further pH increases resulted in lowering of the absorbance values to a pH of approximately 7-8. Near this point, the absorbance values then increased with increasing pH values. A duplicate run after 3 days showed the same trend. The reason for the higher absorbance at pH 5.0 and after pH 8.0 was not pursued as it falls out of the scope of this project. However, this may be due to the ionization of different chromophores at different pH values.

The rate of absorbance change per unit of pH change was found to be greater at the lower wavelengths, because this is the region of more intense absorption and is, therefore, more sensitive to small variations.

Effect of Time on Absorbance

Absorption spectra of the untreated sample at pH 7.6 were run after storing the samples at room temperature for 1, 3, 6, and 24 days. All samples exhibited an increase in absorbance as the wavelength decreased (700 to 230 nm). Three wavelengths (420, 280, and 254 nm) were chosen for further study. Wavelength 420 nm was used because it is in the high energy area in the visible spectrum and 280 nm was selected because this is the standard area of absorption for lignin[7]. The reasons for using 254 nm were circumstantial. Initial work at 254 nm was done because this was the only continuous monitoring device at hand when this work was started. However, a correlation between 254 and 280 nm was established, thus justifying continued use of 254 nm for monitoring kraft mill effluents.

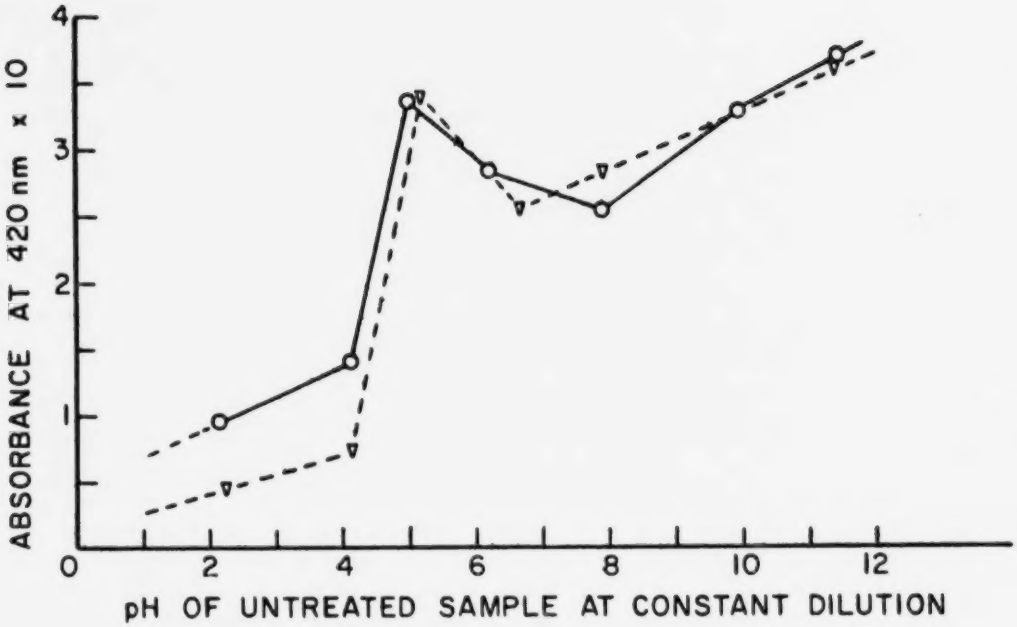

Figure 2. Effect of pH on Absorbance (at 420 nm) of Untreated Waste

The absorbance values measured at the above 3 wavelengths (Figure 3) increased up to a storage time of 3 days and then decreased, first sharply between 3 and 6 days and then slowly between 6 and 24 days. The exact reason for such a behavior is not known but it could be due to the possibility that limited oxidation might tend to increase color.

The observations so far suggest that in order to be able to compare different wastes, the spectrophotometric study should be performed at the same pH and that in case the liquid wastes cannot be analyzed immediately upon receipt, they should be stored in a state in which minimum possible changes occur. The storage conditions are discussed in the following text under waste storage.

Waste Storage

Reductions in color were observed during the storage of wastes in the liquid form over longer periods, even at 5°C. Freeze drying of the colored wastes was found to prevent appreciable changes in color bodies during storage. Freeze-dried material was readily soluble in water.

It was thought that any appreciable physical change occurring in color bodies during freeze drying could be detected by observing changes in the sedimentation coefficient values of the color bodies before and

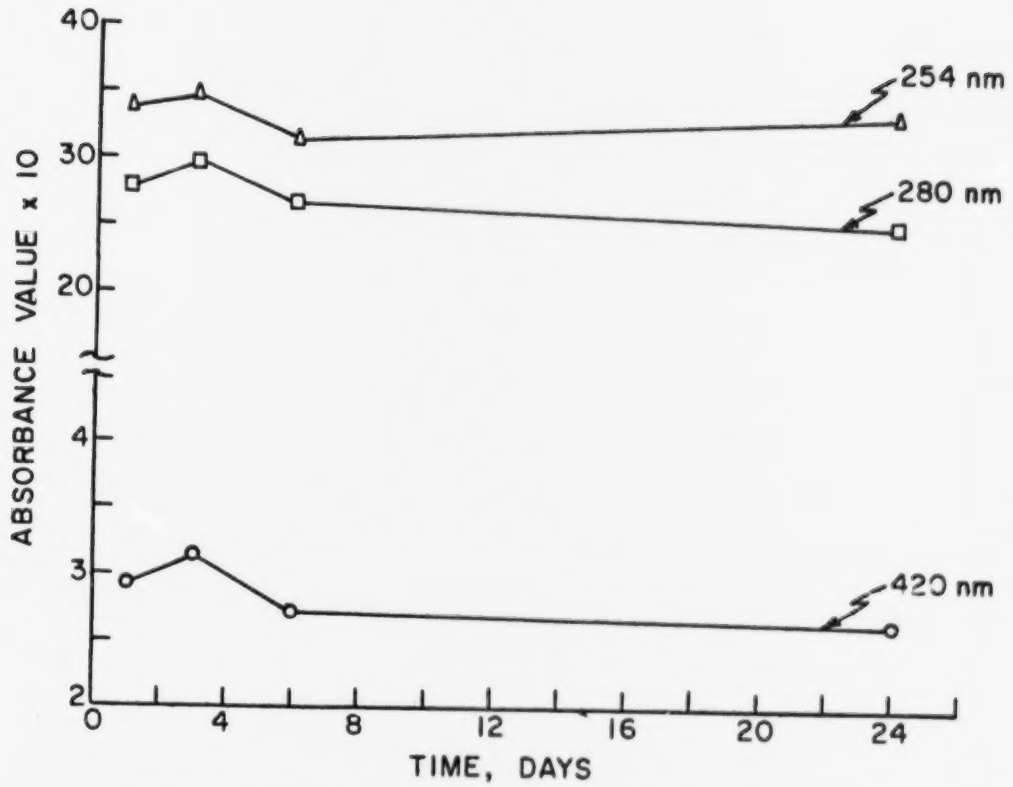

Figure 3. Effect of Storage on Absorbance (at pH 7.6) of Untreated Waste

after freeze drying. The sedimentation coefficient, defined as the velocity of sedimenting molecule per unit field, is a function of the anhydrous molecular weight of the sedimenting substance and the partial specific volume of the solute. It decreases with decrease in molecular weight, and increases in hydration of the sedimenting molecule.

The sedimentation coefficients were determined according to the method described by Schachman[8] with the ultracentrifuge. The lapse time between the measurements of samples before and after freeze-drying was about 4-5 days. The results indicated that, although some variation occurred, the untreated samples showed little average decrease in sedimentation values due to the freeze-drying step, whereas the lime-treated samples showed consistently an average decrease of over 45 percent. Obviously, either the molecular weight of the substance is decreasing or the size and hydration of the molecule is increasing. Because no change in color and TOC (before and after freeze-drying) was noticed, the reason for the decrease in sedimentation coefficients of the lime-treated samples was not further investigated. It should be pointed out here that, upon redissolution in water, the freeze-dried material gave an opaque colorless sediment which upon emission spectrographic analysis was found to be mainly silica.

Microscopic investigation under polarized light also showed the presence of starch. It is possible that the loss of these materials from the colored solutions resulted in lower sedimentation coefficients of the freeze-dried color bodies.

The handling and freeze-drying of the wastes is explained in the experimental part of this report. Chemical analysis of the freeze-dried color bodies of all samples (untreated-, lime-treated-, and returned-Series) are given in Tables 4, 5, and 6. Calculations showed that no appreciable change in chloride content occurred during lime treatment. The sludge obtained by centrifuging the original and carbonated colored wastes was also freeze-dried and analyzed (data not included in this report). These sludges were found to contain mainly fibers, calcium carbonate, and very low amounts of sodium.

Analytical data on the freeze-dried color bodies did not show any particular trend. Fluctuations in the data were found to be due to carbon dioxide absorption during processing, freeze drying, and conditioning of freeze-dried material. Data calculated on a carbon dioxide-free basis showed lesser variations but still no particular trend was evident.

Aqueous solutions of freeze-dried color bodies were tested for color, absorbance, and total organic carbon (TOC). The plots of color versus organic carbon (Figure 4), color versus absorbance at 254 nm (Figure 5) and absorbance at 254 nm versus organic carbon (Figure 6) gave linear relationships. (The reasons for using 254 nm wavelength have already been mentioned in this report.) Because no color losses were noticed upon freeze drying nor upon longer storage periods in the dry state, all color bodies were, therefore, freeze-dried and stored until used for further study.

TABLE 4

ANALYTICAL DATA ON FREEZE-DRIED COLOR BODIES FROM UNTREATED WASTE WATER

Sample Designation	U2-1C	U3-1C	U4-1C	U5-1C	U6-1C	U7-1C	U8-1C	Range	Avg
Sodium, percent	24.8	23.4	24.4	25.4	24.0	23.8	28.8	23.4-28.8	24.9
Calcium, percent	0.3	0.5	0.1	0.2	0.1	0.1	0.2	0.1-0.5	0.2
Nitrogen, percent	0.05	0.07	0.1	0.06	--	--	--	0.05-0.1	0.07
Chloride, percent	--	--	0.5	0.7	0.82	0.6	0.96	0.5-0.96	0.71
Organic Carbon, percent	10.4	10.9	16.6	17.4	18.1	19.6	9.6	10.4-19.6	14.7
Total Solids, g/100 ml	0.12	0.09	0.11	0.11	0.09	0.17	0.12	0.09-0.17	0.11
Fixed Solids (Ash), percent	84.0	78.3	74.3	78.3	73.7	69.1	85.5	69.1-85.5	77.6
Volatiles, percent	16	21.7	25.7	21.7	26.3	30.9	14.5	16-30.9	22.4
Carbonate, percent									
in Total Solids	18.6	6.4	16.4	16.6	11.4	12.5	7.6	6.4-18.6	12.8
in Fixed Solids	--	9.4	25.1	23.1	17.2	24.6	10.0	9.4-25.1	18.2

All values calculated on the basis of od total solids taken as 100 percent.

TABLE 5

ANALYTICAL DATA ON FREEZE-DRIED COLOR BODIES FROM LIME-TREATED WASTE WATER

Sample Designation	LT2-1C	LT3-1C	LT4-1C	LT5-1C	LT-6-1C	LT7-1C	LT8-1C	Range	Avg
Sodium, percent	28.5	26.6	27.2	28.2	26.4	29.1	28.6	26.4-29.1	27.8
Calcium, percent	0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1-0.2	<0.1
Nitrogen, percent	0.04	0.04	0.4	0.04	--	--	--	0.04-0.4	0.13
Chloride, percent	--	--	0.6	0.79	0.98	0.6	0.78	0.6-0.98	0.73
Organic Carbon, percent	5.5	6.00	11.2	10.3	11.3	11.1	6.3	5.5-11.3	9.0
Total Solids, g/100 ml.	0.11	0.08	0.1	0.09	0.095	0.124	0.11	0.08-0.124	0.1
Fixed Solids (Ash), percent	90.6	52.2	81.4	84.4	82.5	83.4	90.2	52.2-90.6	80.7
Volatile, percent	9.4	47.8	18.6	15.6	27.8	16.6	9.8	9.8-47.8	19.3
Carbonate, percent									
In Total Solids	18.6	6.4	16.4	16.6	11.4	17.1	9.8	6.4-18.6	13.8
In Fixed Solids	--	9.4	25.1	23.1	17.2	24.4	11.0	9.4-25.1	15.0

TABLE 6

ANALYTICAL DATA ON FREEZE-DRIED COLOR BODIES FROM RETURNED WASTE WATER

Sample Designation	R2-1C	R4-1C	R5-1C	R7-1C	R8-1C	Range	Avg
Sodium, percent	29.4	27.5	27.4	27.3	29.2	27.3-29.4	28.2
Calcium, percent	0.3	<0.1	<0.1	0.1	<0.1	<0.1-0.3	0.1
Nitrogen, percent	0.08	0.06	0.08	--	--	0.06-0.08	0.07
Chloride, percent	--	0.6	0.9	0.5	0.52	0.5-0.9	0.63
Organic Carbon, percent	12.0	10.3	13.7	13.1	11.5	10.3-13.7	12.1
Total Solids, g/100 ml	0.13	0.1	0.13	0.168	0.17	0.1-0.168	0.12
Fixed Solids (Ash), percent	80.5	83.5	81.1	79.8	82.5	79.8-83.5	81.5
Volatile, percent	19.5	16.5	18.9	20.2	17.5	16.5-20.2	18.5
Carbonate, percent							
In Total Solids	26.0	20.6	18.0	20.2	19.7	18.0-26.0	20.9
In Fixed Solids	--	24.8	25.7	26.5	24.4	24.4-26.5	25.3

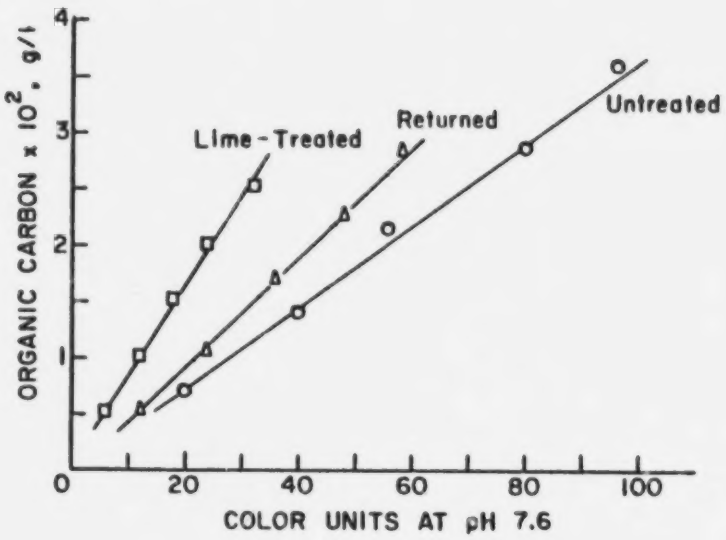

Figure 4. Correlation of Total Organic Carbon with Color Units (at pH 7.6) of Freeze-Dried Untreated, Lime-Treated, and Returned Wastes

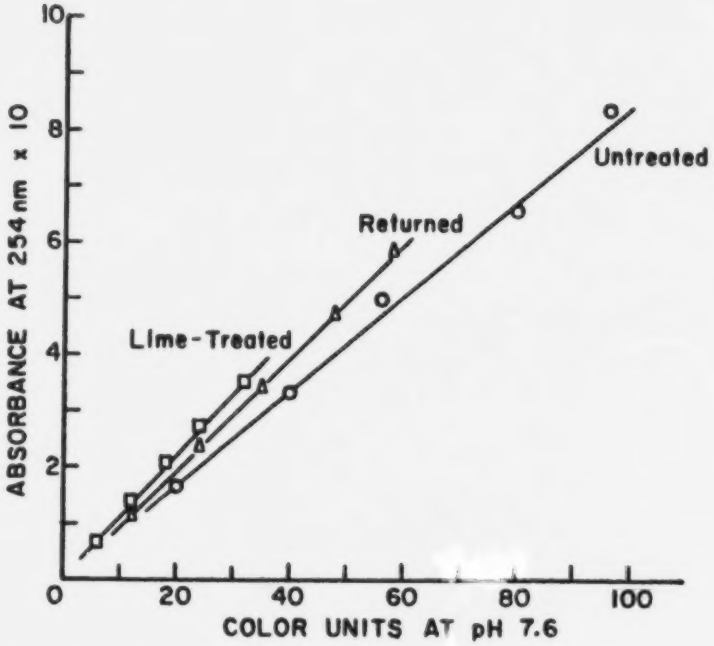

Figure 5. Correlation of Absorbance (at 254 nm) with Color Units (at pH 7.6) of Freeze-Dried Untreated, Lime-Treated, and Returned Wastes

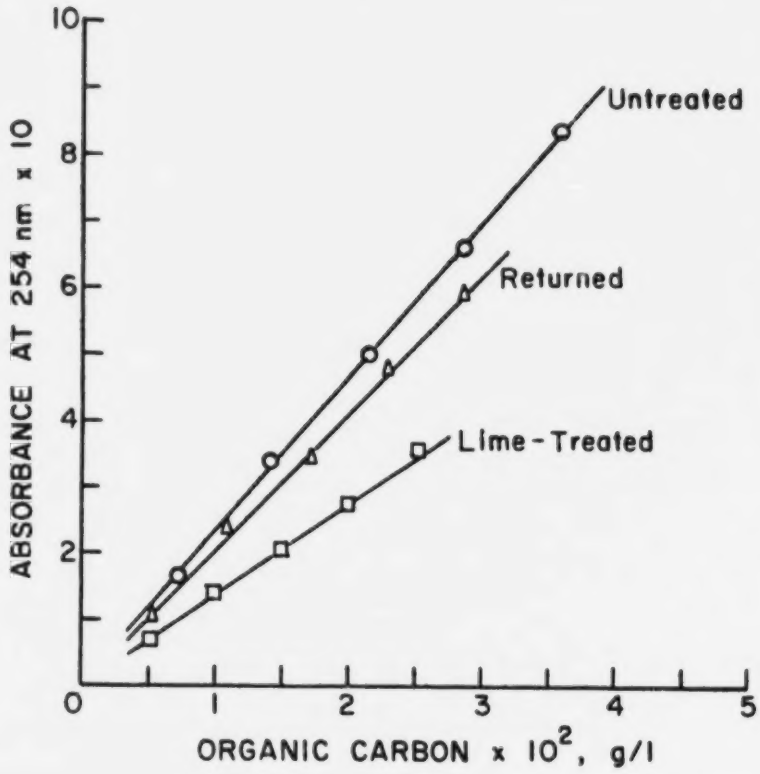

Figure 6. Correlation of Total Organic Carbon with Absorbance (at 254 nm) of Freeze-Dried Untreated, Lime-Treated, and Returned Wastes

SECTION V

ISOLATION AND FRACTIONATION OF COLOR BODIES

The freeze-dried color bodies contained a large amount of ash. They seem to occur naturally as sodium salts. For characterization of color bodies, it was desirable to isolate them as free color bodies and to separate them from the inorganic constituents. Ion exchange resins, dialysis, sorption on carbon and on synthetic resin, gel permeation chromatography, and paper chromatography were tested as means for accomplishing the desired goal.

Ion Exchange Resin

Ion exchange resins are often used for removal of mineral constituents from water. When the original wastes or waste fractions from a Bio-Gel column were passed through a column of Amberlite IR-120 (hydrogen form), most of the cations were removed from solution and most of the color bodies remained in solution. Sometimes, insoluble materials separated from the aqueous solution. This could be prevented by addition of up to one volume of 95 percent ethanol per volume of aqueous solution. Sulfates and chlorides in the wastes were converted to sulfuric and hydrochloric acids by the resin and remained with the color bodies in the eluates of a cation exchange column. Although Amberlite IR-120 seemed to be satisfactory for removal of cations, a subsequent treatment to remove mineral acids was needed.

Mixed bed resins were used to remove both cations and anions in a single treatment. When solutions of the original wastes were passed through a column of the mixed bed resin, Amberlite MB3, 15 to 20 percent of the color was retained by the column and could not be recovered. In addition, the solids passing through the column still contained 3-5 percent ash. This was mainly silica, but its presence in the isolated color bodies was undesirable.

Amberlite MB3 is a mixture of strong exchange resins, Amberlite IR-120 and IRA-410, and thus it is possible that some of the color bodies were sorbed on the strong anion exchange resin. However, when the waste was treated with Amberlite IR-120 and then with the weak anion exchange resin, namely IR-45, 15 to 20 percent of the color was still retained by the anion exchange resin. But in this case, at least a part of the sorbed color could be removed by elution with ammonium hydroxide giving a solution containing ammonium salts with excess of ammonium hydroxide. Presumably, the ammonia could have been removed by evaporation followed by treatment with Amberlite IR-120 to remove ammonium ions but this was not done. A remaining difficulty in any case would still be the presence of silica in the demineralized solutions.

Dialysis

Dialysis was tested as a means of isolating the color bodies. Cellulose acetate tubing having an average pore size of 40 A. was used for dialysis at pH 10.3, 7.2, and 2.9. About 50 percent of the color passed through the tube with the mineral constituents.

When a solution of the untreated waste was first treated with Amberlite IR-120 to remove cations, and then was dialyzed against distilled water using a similar tube, about 80 percent of the original color remained in the dialysis bag and presumably was free of at least the main part of the inorganic constituents. Since we were searching for a procedure which would recover all of the color bodies, work on dialysis was discontinued.

Sorption on Carbon

Carbon is often suggested for removal of color from waste waters especially the small amounts of color remaining after other treatments. Attempts to use Darco Grade 60 (Atlas Chemical Industries, Wilmington, Delaware) for isolation of color bodies from the original wastes were not successful.

When untreated waste was treated with this carbon and filtered, the aqueous filtrate and washings had very light tan color and contained 8 percent of the starting material by weight. The carbon containing color bodies was washed first with 50 percent aqueous ethanol and then with 50 percent pyridine. The aqueous ethanol eluate contained 8.7 percent and the aqueous pyridine eluate 5.6 percent of the starting material. The color fractions, however, were contaminated with a small undetermined amount of colloidal carbon which could not be removed by filtration. In addition, some color was irreversibly sorbed on the carbon.

Sorption on Synthetic Resin

Information supplied by the Rohm & Haas Company representatives indicated that the Amberlite XAD-2 resin is capable of removing color from waste waters. When an aqueous solution of the original waste was passed through an XAD-2 column, no appreciable color was removed. But when the solution was first decationized by IR-120 resin and then passed through a bed of Amberlite XAD-2 resin about one-third of the color was retained and could be removed from the column by elution with 50 percent ethanol.

Gel-Permeation Chromatography (GPC)

GPC was attempted as a means for obtaining ash-free color bodies from both untreated and lime-treated decker wastes. Bio-Gel P-2 column having an exclusion limit of molecular weight 2600, a total bed volume of 420 ml and an approximate void volume of 162 ml was used for this purpose.

Fifteen ml of 10 percent solutions of color bodies from the untreated and lime-treated wastes were separately fractionated in the above column at flow rates of 0.2 to 0.3 ml/min. Distilled water was used as eluent. The eluate was monitored by a UV source at 280 nm because this is the standard area of absorption for lignin, and the fractions were collected at ten-minute intervals. Seventy-seven to ninety fractions were collected in this way and analyzed for color, total solids, fixed solids, volatiles (by difference), absorbance at 280 nm, and pH. Because the absorbance values followed the same trend as that of color, these are not plotted here.

The data obtained for each fraction were calculated as a percentage of the respective parent sample (untreated or lime treated) and then divided by the volume of that fraction to obtain the percentage of color per milliliter in each fraction. The total solids, fixed solids, and volatiles were all expressed as percentages of the total solids of the parent sample. Figures 7 and 8 are plots of these parameters and of pH against elution volume.

A general comparison of these figures shows that:

a. Curves of untreated and lime-treated wastes display two major peaks.
b. The total- and fixed-solids of untreated and lime-treated wastes elute at approximately the same elution volume.
c. One of the peaks of the volatile curve of the lime-treated waste at higher elution volume does not coincide with that of the color curve as is the case with untreated wastes.

Figure 9 shows plots of color-to-volatile ratio of untreated and lime-treated waste fractions *versus* their respective elution volumes. A general decrease in these ratios is observed as the elution volume increases. The ratios of the lime-treated fractions, as expected, are lower than those of the untreated fractions, indicating that most of the highly colored carbon is removed during lime treatment.

In order to further evaluate the degree of removal, ratios of the maximum values of color, volatile- and fixed-solids at two major elution volumes of untreated and lime-treated wastes were calculated and the results are given in Table 7. A significant decrease in these ratios after lime treatment indicates that comparatively higher amounts of color bodies

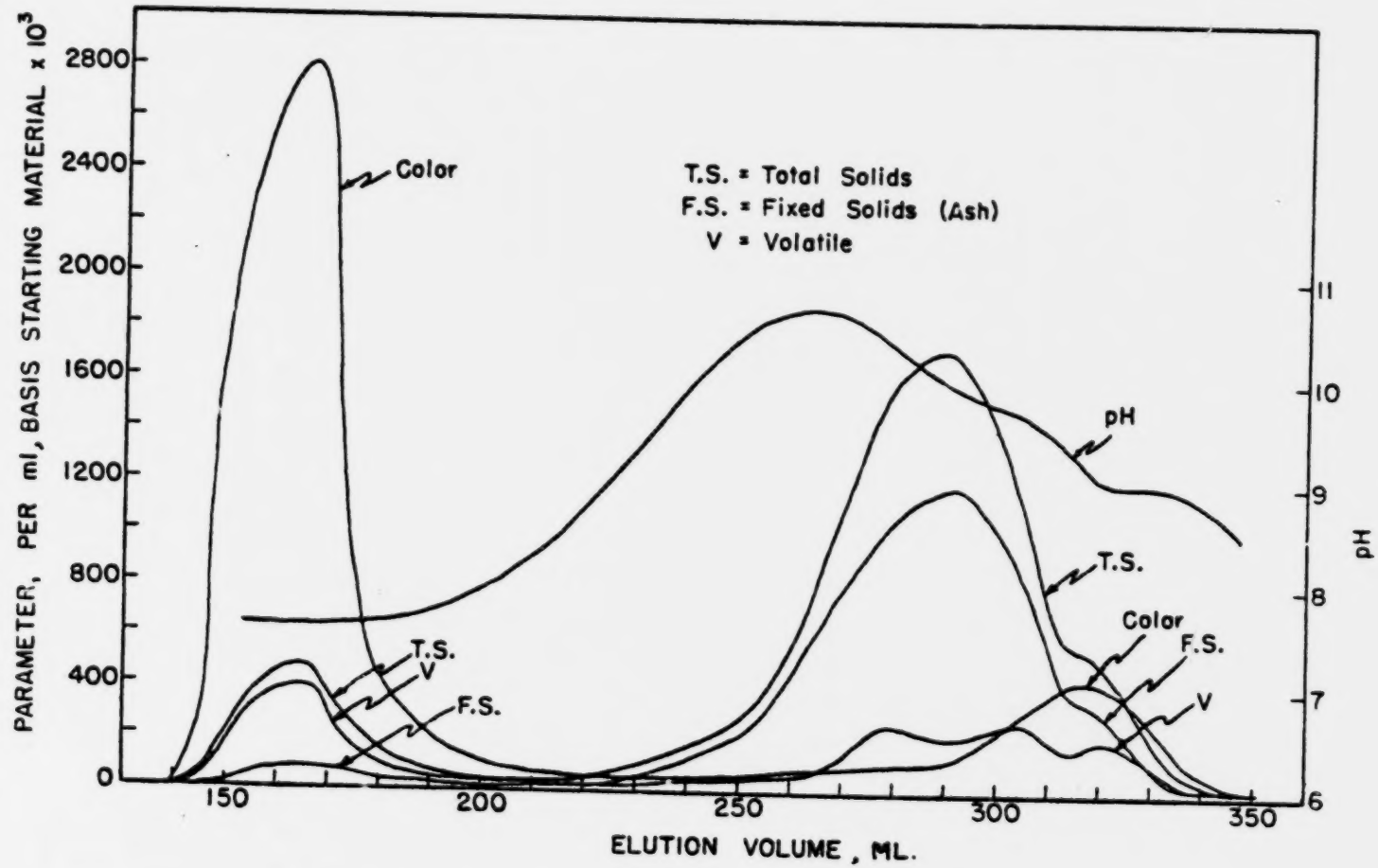

Figure 7. Fractionation of Untreated Dilute Kraft Mill Decker Waste. Parameter Calculated as Percent of Untreated Waste Present in One ml of the Collected Fraction

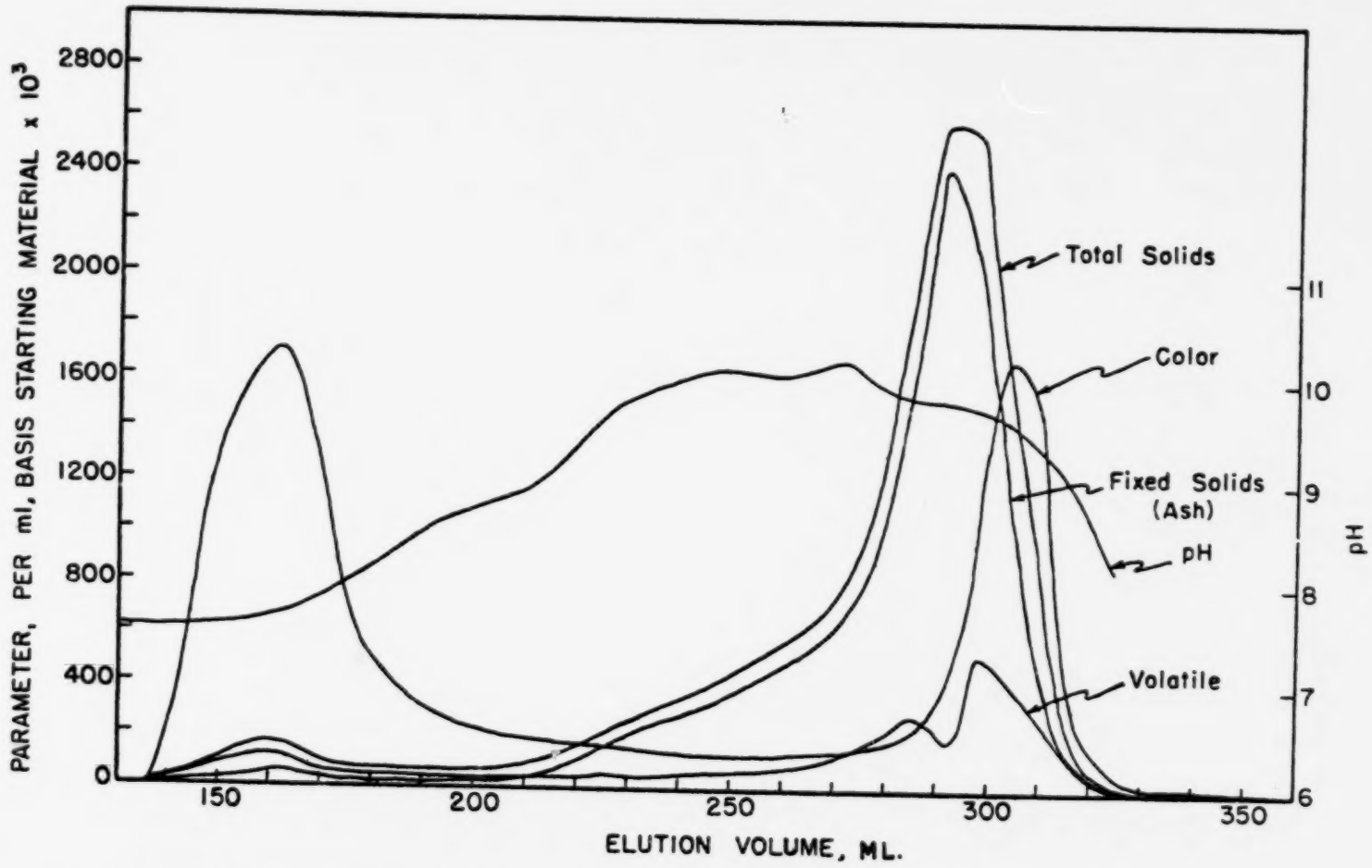

Figure 8. Fractionation of Lime-Treated Dilute Kraft Mill Decker Waste. Parameter Calculated as Percent of Lime-Treated Waste Present in One ml of the Collected Fraction

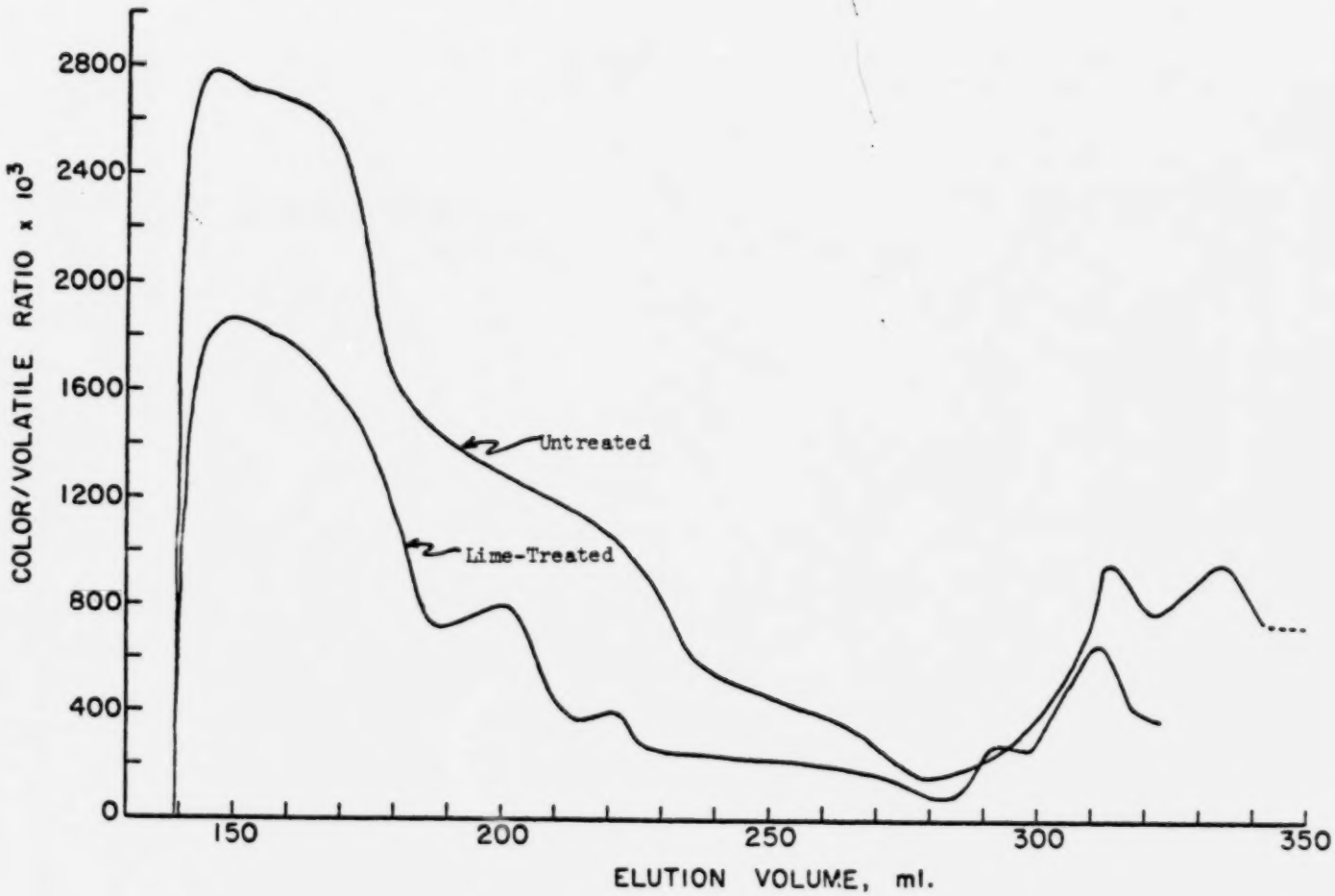

Figure 9. Fractionation of Untreated and Lime-Treated Dilute Kraft Mill Wastes. Ratio of Color Units to Volatiles x 10^3 Versus Elution Volume

eluting at lower elution volumes (higher molecular weights) are removed during lime treatment.

TABLE 7

EFFECT OF LIME TREATMENT ON WASTE FRACTIONS

	Untreated			Lime Treated		
	Maximum Value at Elution Volume of			Maximum Value at Elution Volume of		
	167 ml (a)	320 ml (b)	Ratio (a)/(b)	162 ml (a)	305 ml (b)	Ratio (a)/(b)
Color Units	24,000	3,600	6.7	3,000	3,000	1.0
Volatile, percent	2.65	1.39	2.8	67	49.3	1.35
Fixed Solids, percent	0.46	2.16	0.21	0.36	6.8	0.05

As the main aim of GPC, at this point, was to obtain ash-free color bodies, the fractionated untreated and lime-treated color bodies were combined according to the following code to give three large fractions in each case, and analyzed for ash, volatiles, sodium, and calcium.

Combined Fractions	Approximate Elution Volume, ml
Untreated (A)	Between 123 to 195
Untreated (B)	Between 195 to 293
Untreated (C)	Between 293 to end of colored fraction
Lime-treated (A)	Between 120 to 193
Lime-treated (B)	Between 193 to 283
Lime-treated (C)	Between 283 to end of colored fraction

The weight average molecular weight (M_w) was also determined by the ultracentrifuge and results are given in Table 8. The molecular weights of the middle fractions (B) are the lowest in both cases. These fractions also contain the highest amounts of ash which is probably responsible for low M_w values. It should be noted that in extremely complex and heterogeneous mixtures, such as these, the M_w values should not be taken as absolute values.

The data further indicate that, although fractions containing color bodies of different molecular weights and sizes could be obtained by GPC, it was not a very effective method for giving ash-free color bodies under these conditions.

TABLE 8

ANALYSIS OF FRACTIONATED COLOR BODIES

Combined Fractions		Fixed Solids (Ash), percent	Volatile, percent	Sodium,[a] percent	Calcium,[a] percent	M_w
Untreated	(A)	26.8	73.2	9.1	0.2	11,400
	(B)	89.0	11.0	28.3	0.1	74
	(C)	71.7	28.3	21.5	<0.1	124
Lime Treated	(A)	48.7	51.3	13.3	0.27	760
	(B)	92.9	7.1	32.9	<0.1	70
	(C)	79.9	20.1	26.2	0.1	85

[a]Analyzed in ash and calculated on respective o.d. fraction.

Paper Chromatography

Paper chromatography was also tried. The chromatograms produced light tan-colored bands and zones which were separated and eluted to yield seven fractions. Although some fractions were more highly colored than others, all fractions carried tan to brown coloration. Furthermore, the inorganic materials appeared to be spread over several fractions. For this reason this method was also abandoned.

In order to further deash the color bodies, a combination method of acidification and GPC was developed.

Acidification and Gel Permeation Chromatography

The effluent color was pH dependent. A decrease in pH decreased the color and also precipitated some color bodies.

Although most of the color remained in solution when a dilute solution of the waste was acidified, up to 80 percent of the color bodies could be precipitated from a concentrated solution (13-20 percent) of the untreated wastes. In addition, a large portion of the color remaining in

the acid solution could be isolated by first sorbing it on Amberlite XAD-2 resin and then desorbing with aqueous ethanol. These techniques were used for the isolation of acid-insoluble and acid-soluble color bodies from the untreated and lime-treated freeze-dried solids. Non-recoverable color bodies have been reported as losses. The results are given in Table 9.

TABLE 9

PERCENTAGE OF YIELD AND REMOVAL BY LIME OF UNTREATED AND LIME-TREATED WASTE FRACTIONS

Fractions	Untreated Waste Yield, %		Lime-Treated Waste Yield, %		Removal[c], %	
	Color[a]	TOC[b]	Color	TOC	Color	TOC
Original Waste	100	100	14.0	42.8	86.0	57.2
Acid-Insoluble	63	59	3.7 (26)	3.6 (8.4)	94.3	94.0
Acid-Soluble	30	18	7.7 (55)	10.2 (23.8)	74.5	43.4
Loss (by difference)	7	23	2.6 (19)	29.0 (67.8)	--	--

All values (except in parentheses) are calculated on the original untreated waste taken as 100.

Values in parentheses are based on original lime-treated waste taken as 100.

[a] A.P.H.A. color units.

[b] Total organic carbon.

[c] Percentage of removal was calculated on the basis of their respective untreated fraction taken as 100.

Table 9 shows that 86 percent of total color and about 57 percent TOC are removed by lime treatment, indicating that the remaining 43 percent TOC contributes to only 14 percent of the original color. It is possible that part of this TOC is in the form of noncolored carbohydrate degradation products, resin acids, etc. The data also indicate that the acid-insoluble components of mill wastes lost 94.3 percent color and 94.0 percent TOC, whereas the acid-soluble components lost only 74.4 percent color and 43.4 percent TOC during lime treatment.

Table 9 further shows that combined color recoveries of the acid-insoluble and acid-soluble components were 93 percent (63 + 30) in the case of untreated wastes and 81 percent (26 + 55) in the case of lime-treated wastes. The corresponding TOC recoveries were 77 percent (59 + 18) and 32.2 percent (8.4 + 23.8), respectively. This indicates that 7 percent color and 23 percent TOC in the case of untreated waste compared to 19 percent color and 68 percent TOC in the case of lime-treated waste were nonrecoverable and remained in the acid solution. These materials were probably of very low molecular weights.

The acid-insoluble and acid-soluble color bodies of both untreated and lime-treated wastes were fractionated into nine to twelve fractions using the Bio-Gel P-2 column (200 cm long and 2.5 cm in diameter) having an exclusion limit of molecular weight 2600. The first fraction, "A," from each run was further fractionated into three to seven fractions using the Bio-Gel P-60 column (100 cm long, 2.5 cm diameter) having an exclusion limit of molecular weight 60,000. Details are given in the experimental part of this report.

All fractions obtained from the gel columns were analyzed for color, TOC, and absorbance at 280 nm. The data were used for calculating percentage yields and removal of color and TOC by lime in each fraction. Results are given in Tables 10 and 11.

The individual values for Fractions A3 through A7 and D through M were small compared to other fractions and so have been tabulated as combined values for easy reference. The detailed data are given in Appendix I.

Appendix I shows that the amounts of material input and output during fractionation fluctuated and some losses were observed in the mass balance. The calculations of these losses were, however, based on cumulative values of all fractions and so the error per fraction would certainly be a lot smaller. Maximum loss (32 percent) was observed in TOC values when the untreated acid-insoluble fraction "A" was further fractionated on Bio-Gel P-60 column. It is believed that this loss was due to the retention of some low molecular weight material which did not elute out at the collected elution volumes.

In the case of untreated acid-insoluble color bodies (Table 10), 79 percent of the color (49.8 x 100/63) and 55.6 percent of the TOC (32.8 x 100/59) were obtained in Fraction A, whereas in the case of lime-treated acid-insoluble color bodies this fraction contained only 32.4 percent of the color (1.2 x 100/3.7) and 19 percent of the TOC (0.68 x 100/3.6). Worth noting is the fact that the general trend of effective removal of color and TOC by lime treatment decreased below Fraction B.

In the case of untreated acid-soluble color bodies (Table 11), on the other hand, 33 percent color (9.9 x 100/30) and 23 percent TOC (4.2 x 100/18) were obtained in Fraction A, whereas in the case of lime-treated acid-soluble color bodies this fraction contained only 25 percent color (1.9 x 100/7.7) and 19.5 percent TOC (2 x 100/10.2), indicating that

most of the acid-soluble color bodies are of lower molecular weights. Tables 10 and 11 also show that the percentage of removal of acid-soluble color bodies by lime was much lower than that of the acid-insoluble color bodies.

TABLE 10

FRACTIONATION OF ACID-INSOLUBLE COLOR BODIES BY COLUMN CHROMATOGRAPHY
(Material balance of color and TOC)

Fractions	Untreated[a] Acid-Insoluble Color Bodies Yield, %		Lime-Treated[a] Acid-Insoluble Color Bodies Yield, %		Removal, %	
	Color	TOC	Color	TOC	Color	TOC
Fraction 'A' from P-2 thru Bio-Gel P-60 column						
A1	11.7	6.8	0.67	0.22	94.5	96.8
A2	19.9	9.7	0.38	0.13	98.0	98.7
A3 thru A5[b]	18.2	16.3	0.15	0.33	99.1	98.1
Acid-insoluble color bodies thru Bio-Gel P-2 column						
A	49.8	32.8	1.20	0.68	97.5	98.0
B	7.6	6.5	0.30	0.24	96.0	96.2
C	1.9	1.1	0.18	0.22	90.5	80.0
D thru M[c]	3.7	18.6	2.02	2.46	46.0	86.5
Unfractionated acid-insoluble color bodies	63.0	59.0	3.70	3.60	94.3	94.0

[a] Percentages of yield are calculated on the basis of untreated original waste.

[b] Calculated by difference so that values for A = (A1+A2+A3 thru A5).

[c] Calculated by difference so that values for unfractionated acid-insoluble color bodies = (A+B+C+D thru M).

Our experience has shown that GPC runs could not be quantitatively duplicated. However, they showed similar trends. In order to compare fractions of different wastes with each other and to minimize the experimental error, especially because there was no clear-cut demarcation line between the two adjacent fractions, the data in Appendix I were divided by their respective fraction volumes and the values per ml thus obtained were plotted against eluate fractions in Figures 10 to 13.

Absorbance value at 280 nm for each fraction was also measured and when plotted as above, gave a pattern similar to that of color and, therefore, is not included in this report.

TABLE 11

FRACTIONATION OF ACID-SOLUBLE COLOR BODIES BY COLUMN CHROMATOGRAPHY
(Material balance of color and TOC)

Fractions	Untreated[a] Acid-Soluble Color Bodies Yield, %		Lime-Treated[a] Acid-Soluble Color Bodies Yield, %		Removal, %	
	Color	TOC	Color	TOC	Color	TOC
Fraction 'A' from P-2 thru Bio-Gel P-60 column						
A1	0.8	0.6	0.07	0.06	91.2	90.0
A2	1.2	1.0	0.13	0.25	89.0	75.0
A3 thru A7[b]	7.9	2.6	1.7	1.69	78.5	35.0
Acid-soluble color bodies thru Bio-Gel P-2 column						
A	9.9	4.2	1.9	2.0	80.8	52.5
B	7.5	5.0	0.7	1.1	90.6	78.0
C	3.4	2.8	1.5	2.5	56.0	10.7
D thru M[c]	9.2	6.0	3.6	4.6	61.0	23.4
Unfractionated acid-soluble color bodies	30.0	18.0	7.7	10.2	74.5	43.4

[a] Percentage yields are calculated on the basis of untreated original waste.

[b] Calculated by difference so that values for A = (A1+A2+A3-A7).

[c] Calculated by difference so that values for unfractionated acid-soluble color bodies = (A+B+C+D thru M).

The dotted areas between the untreated and lime-treated curves in Figures 10, 11, 12, and 13 correspond to the amounts of color, and TOC removed by the lime-treatment process. A comparison of these figures indicates that lime treatment removes more color and TOC from the acid-insoluble color bodies than acid-soluble color bodies. These figures also show that the TOC patterns for different wastes are not similar to their respective color patterns, indicating the presence of "noncolored" organic carbon in some of these fractions.

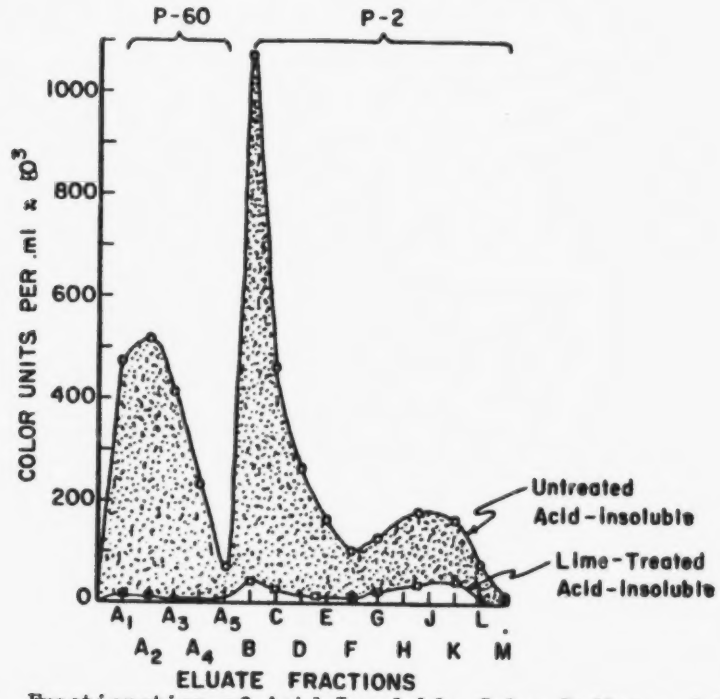

Figure 10. Fractionation of Acid-Insoluble Color Bodies. Color Units Calculated as Percent of Untreated Waste Present in One Ml of the Collected Fraction

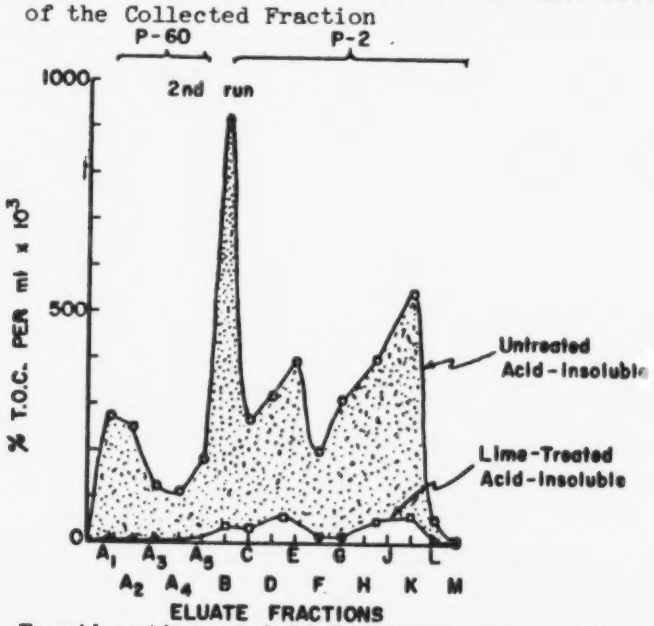

Figure 11. Fractionation of Acid-Insoluble Color Bodies. TOC Calculated as Percent of Untreated Waste Present in One Ml of the Collected Fraction

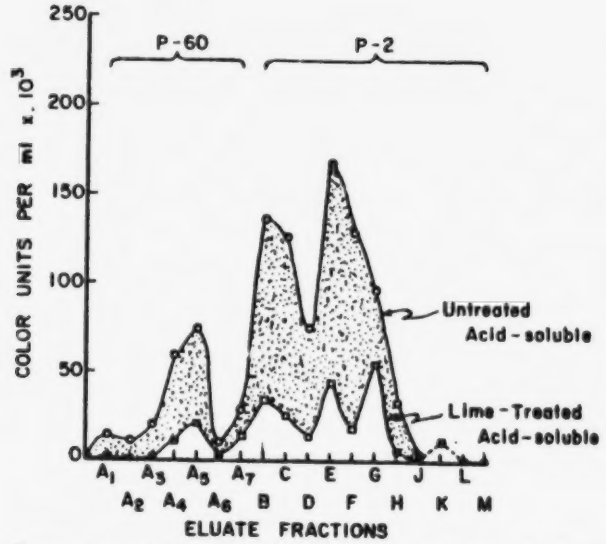

Figure 12. Fractionation of Acid-Soluble Color Bodies. Color Units Calculated as Percent of Untreated Waste Present in One Ml of the Collected Fraction

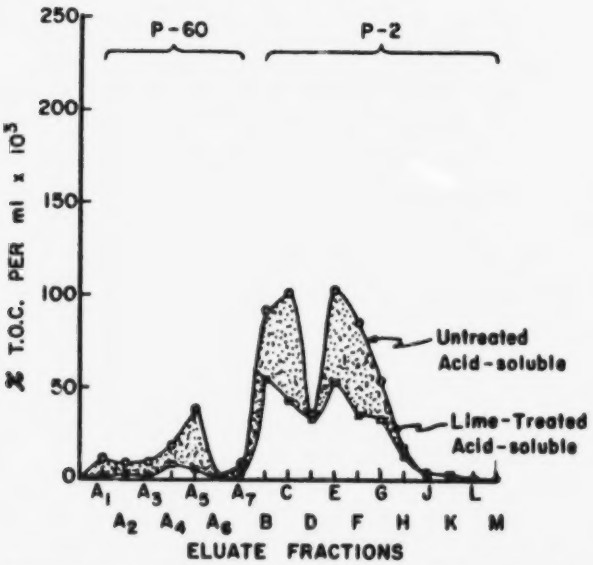

Figure 13. Fractionation of Acid-Soluble Color Bodies. TOC Calculated as Percent of Untreated Waste Present in One Ml of the Collected Fraction

SECTION VI

CHARACTERIZATION OF COLOR BODIES

Elemental Analysis

Acid-insoluble and acid-soluble fractions were isolated from three untreated and two lime-treated wastes. Color of each fraction was determined by the American Public Health Association method[9], and the recovery was calculated on the basis of the original color. Five fractions were analyzed for carbon, hydrogen, methoxyl, nitrogen, and ash. Absorptivities (absorbance/solids in g/l) were determined at 420 nm (a_{420}) as a measure of original color, and at 280 nm (a_{280}) and the maximum near 200 nm (a_{max}) as a measure of the lignin content. The results are summarized in Table 12. Absorptivities for Indulin 'C' and analytical data for an alkali lignin from pinewood are included in the table. Analytical data were not obtained for Indulin C, but the values for the alkali lignin are believed to be good approximations of the composition of Indulin.

The data in Table 12 include three values which may be used as approximate measures of lignin content, namely: methoxyl, absorptivity at 280 nm and absorptivity at the maximum. Calculated ratios of absorptivity at 420 nm (as a measure of color) to each of these are included in the table.

The data suggest that at least most of the color bodies are ligninlike and that they consist of lignins which have been degraded to varying degrees. The lignin in all of the wastes appear to have lost somewhat more methoxyl than Indulin C, with those in the more soluble fractions having lost the greatest amount of methoxyl. The loss in methoxyl of the more soluble fractions was not checked by determining the corresponding increase, if any, in the phenolic group content.

The ratios of the absorptivity at 420 nm to the methoxyl content, the absorptivity at 280 nm and at the 'maximum' suggest that, except for some greater loss of methoxyl, the lignins in the acid-insoluble fractions from the untreated wastes are very similar to the lignins in Indulin C. The lignins in the untreated acid-soluble fractions and those from the lime-treated acid-insoluble and acid-soluble fractions appear to have been more degraded. Goring, *et al.*[10,11] have indicated that, during pulping, the very low molecular weight lignins are not produced by degradation of the high molecular weight lignins. The authors further indicate that one of the two types of protolignins present in softwoods gives very low molecular weight lignins whereas the other gives high molecular weight lignins.

Our use of the word "degraded" is based on the observation that color decreases during the handling and storage of liquid wastes. Such changes

TABLE 12

COMPARISON OF ACID-INSOLUBLE AND ACID-SOLUBLE FRACTIONS WITH INDULIN

(Color Recovery, Analytical Data, and Absorptivity)

Original Waste Fraction	Indulin[b]	U4-1C		U7-1C		U8-1C		LT7-1C		LT8-1C	
		Acid-Ins.	Acid-Sol.	Acid-Ins.	Acid-Sol.	Acid-Ins.	Acid-Sol.	Acid-Ins.	Acid-Sol.	Acid-Ins.	Acid-Sol.
Color Recovery, percent	--	84	14	63	30	46	42	26	55	36	54
Carbon, percent	63.4	55.34	--	56.89	47.92	--	--	51.82	48.30	--	--
Hydrogen, percent	5.6	5.25	--	5.30	4.87	--	--	5.55	5.47	--	--
Nitrogen, percent	--	0.36	--	0.33	0.68	--	--	0.25	0.42	--	--
Ash, percent	--	9.78	--	7.81	6.04	--	--	17.18	4.56	--	--
"Oxygen" by Difference, percent	31.0	29.3	--	29.7	40.5	--	--	25.2	41.2	--	--
Methoxyl (MeO), percent	14.2	11.23	--	8.51	5.20	--	--	4.09	4.37	--	--
a_{420}[a]	1.54	1.38	0.74	1.41	1.25	1.09	0.95	0.72	1.04	0.64	0.92
a_{280}[a]	19.0	16.7	10.5	16.9	12.9	13.2	14.1	10.5	12.1	10.5	12.1
a_{max}[a]	83.2	77.5	51.6	78.0	51.9	73.1	60.6	56.8	50.0	68.4	63.4
a_{420}/MeO Ratio[a]	0.11	0.12	--	0.17	0.24	--	--	0.18	0.24	--	--
a_{420}/a_{280} Ratio[a]	0.081	0.083	0.070	0.083	0.097	0.083	0.067	0.069	0.086	0.061	0.076
a_{420}/a_{max} Ratio[a]	0.018	0.018	0.014	0.018	0.024	0.015	0.016	0.013	0.021	0.009	0.014

[a] a_{420}, a_{280}, a_{max}, are absorptivities at 420 nm, 280 nm, and maximum, respectively.

[b] Analytical data for an alkali lignin from pinewood, absorptivities for Indulin C.

are possibly due to the degradation of color bodies — which are believed to be of lignin origin.

Analysis of Fractions Obtained by Gel Permeation Chromatography (GPC)

Fractions of acid-insoluble and acid-soluble color bodies from the untreated and lime-treated wastes were obtained by GPC, but several of these fractions were very small, especially after keeping aside the amounts required for the estimation of molecular weights.

To provide sufficient material for chemical analysis some adjacent fractions which were similar with regard to their ratios of color to organic carbon were combined to give bulky fractions. Only the acid-insoluble color bodies from the untreated waste, were found to be enough for chemical analysis. Molecular weight (M_w), color yield, color/carbon ratio, carbon, hydrogen, methoxyl and ash data of these bulky fractions are given in Table 13, along with data for acid-insoluble color bodies and an alkali lignin taken from Table 12 (some of the original intermediate fractions were not analyzed).

The variable ash content in Table 13 makes direct comparisons difficult. Since the composition of the ash is unknown, corrections to ash-free basis seems questionable. Instead, ratios of methoxyl to carbon are calculated. The results indicate that gel permeation chromatography resulted in fractionation of chemical classes as well as molecular sizes. The lowest molecular weight fraction had a very low ratio of methoxyl to carbon (0.04) indicating little ligninlike material. All of the fractions probably are mixtures and, thus, a low methoxyl content may be due to a high proportion of nonlignin materials, as well as to the presence of highly degraded lignins. Infrared spectroscopy (see below) has also shown that very soluble colored fractions (low molecular weight) are associated with the carbohydrate material.

Sugar Analyses of Untreated and Lime-Treated Wastes

Sugar analyses of acid-insoluble and acid-soluble color bodies from the untreated and lime-treated wastes and their fractions obtained by gel permeation chromatography were conducted by the method of Borchardt and Piper[12]. The following sugars: rhamnose, arabinose, xylose, mannose, galactose, and glucose, were found and are reported as anhydrous sugars. As the amounts of individual sugars in each fraction were small, only the total sugar values of the major fractions are reported in Table 14. (For detailed data see Appendix II.) Indulin value is included for comparison only.

Table 14 shows that the total amount of sugars present in Indulin is 1.07 percent, in untreated waste 1.51 percent, and in lime-treated waste 2.92 percent (Column I). About 17 percent (100-82.8) sugars of the untreated waste is removed during the lime treatment process, thus contributing to some BOD removal. Column III of the table shows that in the case of the untreated waste 62.5 percent of the sugars are

TABLE 13

ANALYTICAL DATA ON FRACTIONATED ACID-INSOLUBLE COLOR BODIES FROM UNTREATED WASTE

Fractions	Wt Av[a] Mol Wt (M_w)	Color[b], % of original (yield)	Av. Ratio of Color to Org Carbon	Carbon, %	Hydrogen, %	Methoxyl (MeO), %	Ash, %	MeO/C[c]
Fraction 'A' from P-2 thru Bio-Gel P-60 column								
A1 + A2	30,000	31.6	6.8	53.5	5.53	9.6	8.9	0.18
A3	8,000	9.8	11.4	--	--	--	--	--
A4 + A5	5,000	5.9	7.4	48.5	5.29	7.7	13.6	0.16
Acid-insoluble waste thru Bio-Gel P-2 column								
B + C	3,000	9.5	9.2	39.5	4.65	5.2	32.3	0.13
D thru K	<800	6.2[d]	3.3	48.4	5.88	2.1	8.5	0.04
Acid-insoluble waste	<400-30,000	63.0	--	56.9	5.30	8.5	7.8	0.15
Alkali lignin	--	--	--	63.4	5.60	14.2	--	0.22

[a] Approximate values.

[b] Calculated on the basis of untreated waste.

[c] These are weight ratios and not mole ratios of methoxyl to carbon.

[d] Value calculated by difference so that total yield of all fractions = 63.0.

obtained in the acid-insoluble fraction and 32 percent in the acid-soluble fraction. On the other hand, in the case of the lime-treated waste, these percentages are reduced to 6 percent and 19 percent, respectively. A total of about 58 percent of the sugars are not recovered in the acid-insoluble and/or acid-soluble fractions of the lime-treated waste. It is believed that these sugars, probably in polymeric form, are originally attached to the color bodies and during the lime treatment process (pH 12-13) are released in the polymeric form without further degradation (according to Mr. Dickey of the Institute, reducing sugars will be destroyed by lime but polymeric sugars ordinarily will not be touched). These sugars ultimately end up with the nonrecoverable low molecular weight material reported as TOC losses after the acid treatment (see Table 9 and Appendix I).

TABLE 14

SUGAR ANALYSES OF UNTREATED AND LIME-TREATED WASTES

Fractions	Total Sugars, %		
	I	II	III
Indulin	1.07	--	--
Untreated Waste	1.51	1.51	100
Acid-insoluble color bodies	1.60	0.945	62.5
Acid-soluble color bodies	2.69	0.484	32.1
Nonrecoverable (loss)	--	0.08	5.4
Lime-Treated Waste	2.92	1.25	82.8(100)
Acid-insoluble color bodies	2.39	0.09	6.0(7.2)
Acid-soluble color bodies	2.86	0.29	19.2(23.2)
Nonrecoverable (loss)	--	0.87	57.6(69.6)

Column I = sugar values are based on moisture free solids in "individual fractions."

Column II = sugar values are based on moisture free "total solids in untreated waste."

Column III = sugar values are based on "untreated waste sugar" content taken as 100.

The values in parentheses are based on the lime-treated waste taken as 100.

Ultraviolet and Visible Spectra

Ultraviolet and visible spectra of Indulin 'A' and acid-insoluble and acid-soluble fractions isolated from the untreated and two lime-treated wastes were determined at a pH of about 7.6.

Absorptivity values from these spectra were calculated at definite wavelengths and the results of untreated and lime-treated series are plotted in Figures 14 and 15.

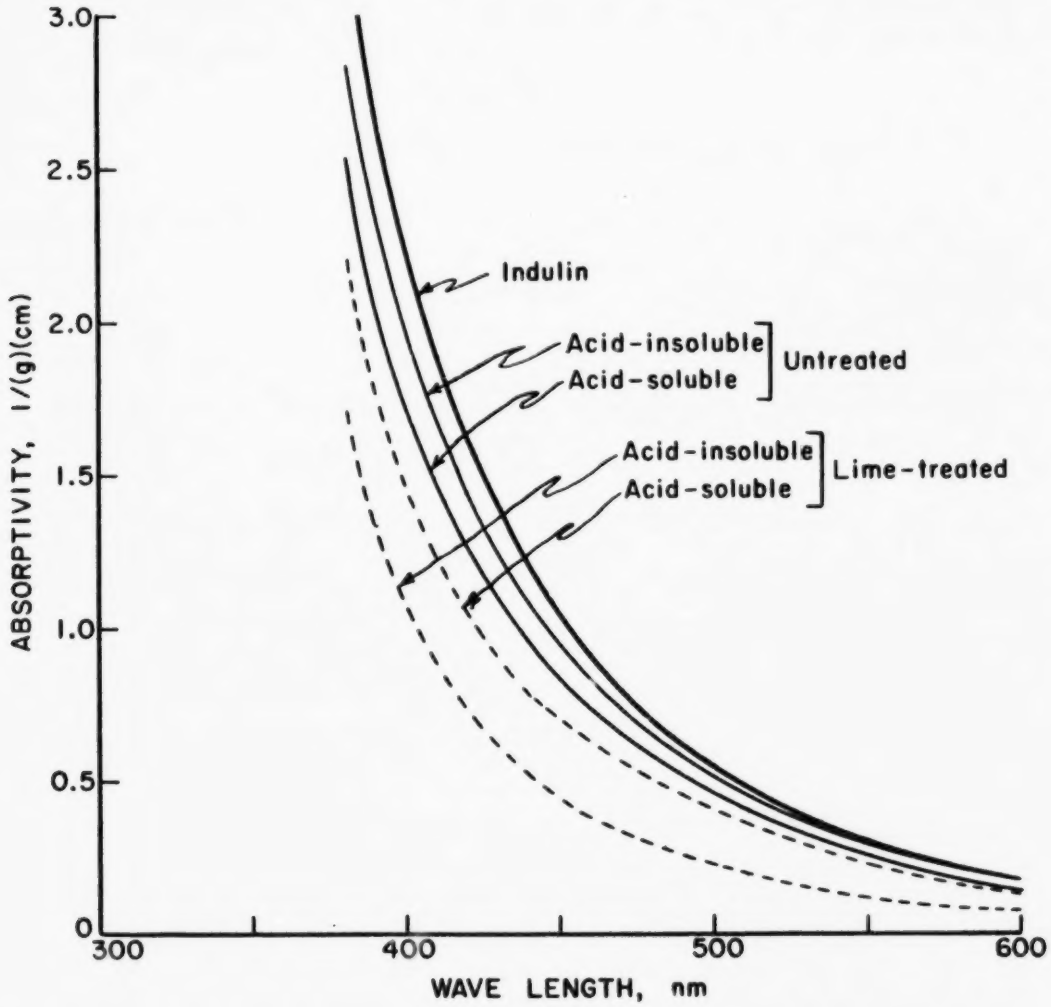

Figure 14. Absorptivity Versus Wavelength (Visible Range) of Indulin "A," Acid-Insoluble and Acid-Soluble Color Bodies of Untreated and Lime-Treated Kraft Mill Decker Wastes

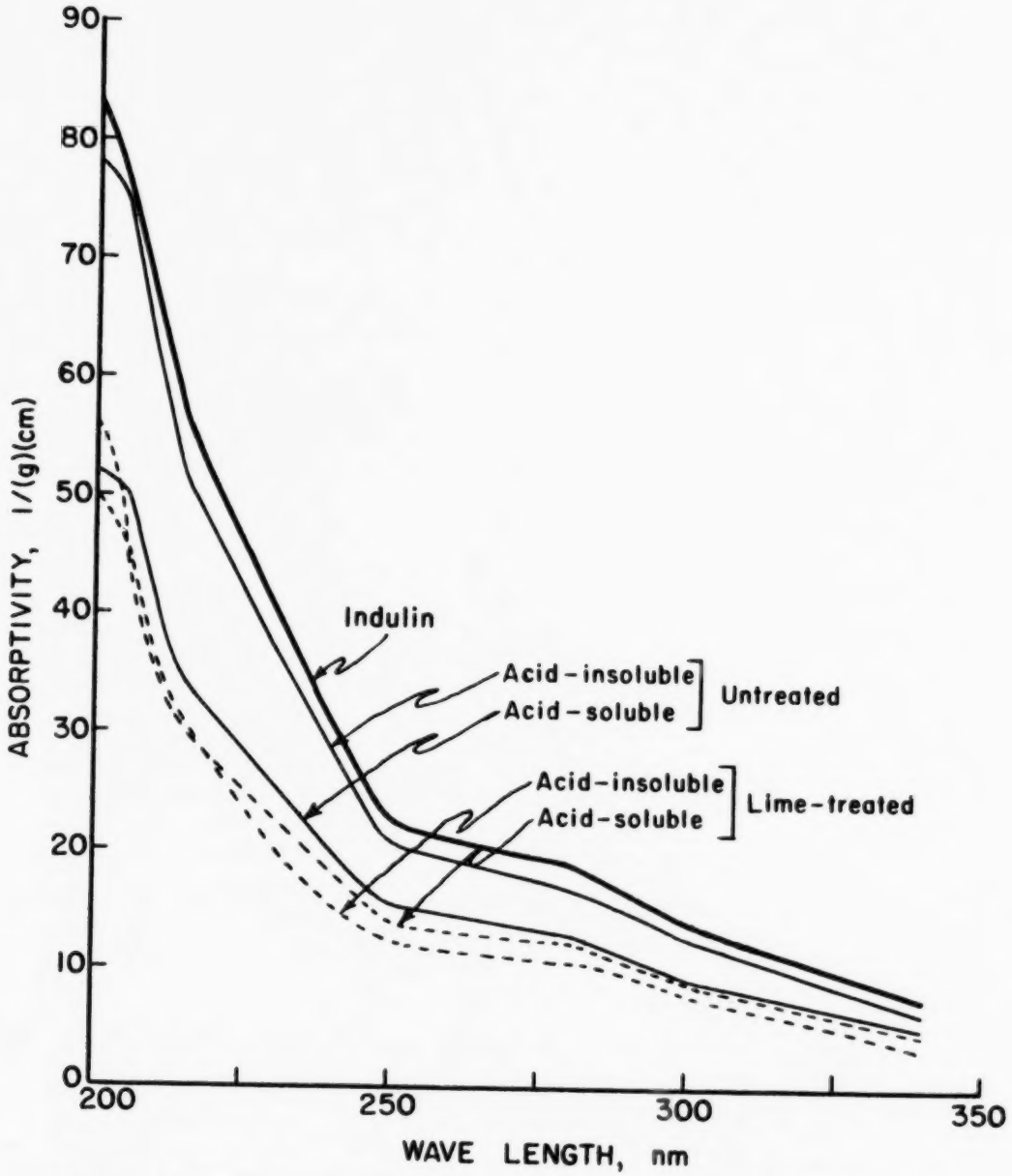

Figure 15. Absorptivity Versus Wavelength (Ultraviolet Range) of Indulin "A," Acid-Insoluble and Acid-Soluble Color Bodies of Untreated and Lime-Treated Kraft Mill Decker Wastes

Figure 14 shows that in the visible range all samples gave simple absorption curves and exhibited an increase in absorptivity as the wavelength decreased. Comparatively, the lime-treated color bodies showed lower absorptivity values than the untreated color bodies. However, the lime-treated acid-insoluble color bodies showed the lowest absorptivity values, even lower than acid-soluble color bodies. This is not surprising as the lime-treated acid-insoluble color bodies contained only 3.7 percent of the original color and lime-treated acid-soluble color bodies contained 7.7 percent of the original color (see Table 9).

In the ultraviolet range (Figure 15) one reaches the same conclusions as in the visible range except that here the characteristic absorption bands at 205 nm and 280 nm are obtained.

It can be said that all fractions contain ligninlike color bodies. The differences in absorptivity values can be due to differences in ash contents and different levels of degradation of color bodies.

Infrared Spectra

Infrared (IR) spectra were determined for acid-insoluble and acid-soluble components of both untreated and lime-treated wastes (Figure 16). The IR spectra were analyzed to see whether or not important functional group differences were associated with the differences in the treatment prior to isolation. It should be realized that detailed interpretation of many of the absorption bands is not possible because of the complexity of the molecular system, uncertainties always present in comparison of solid state spectra, and the interference by impurities (elemental analyses revealed ash contents from 4.56 to 17.18 percent).

In the following discussion, frequent reference will be made to comparisons of sample spectra with a spectrum of Indulin A.

Acid-Soluble Samples (Untreated and Lime-Treated)

The spectra of untreated and lime-treated samples were nearly identical; the differences that do exist are solely minor differences in the relative intensities of a few bands, and it would be unwise to assign a specific structural difference as the cause of these intensity changes. It is possible, however, to comment on the absorption in certain spectral regions and the implications to the structural question for the acid-soluble samples.

1. OH and CH stretch (2500-3600 cm^{-1})

   It is impossible to make meaningful comparisons of the OH intensities from one sample to another because of the variable amounts of water in the samples. However, there is one consistent difference between the Indulin A sample

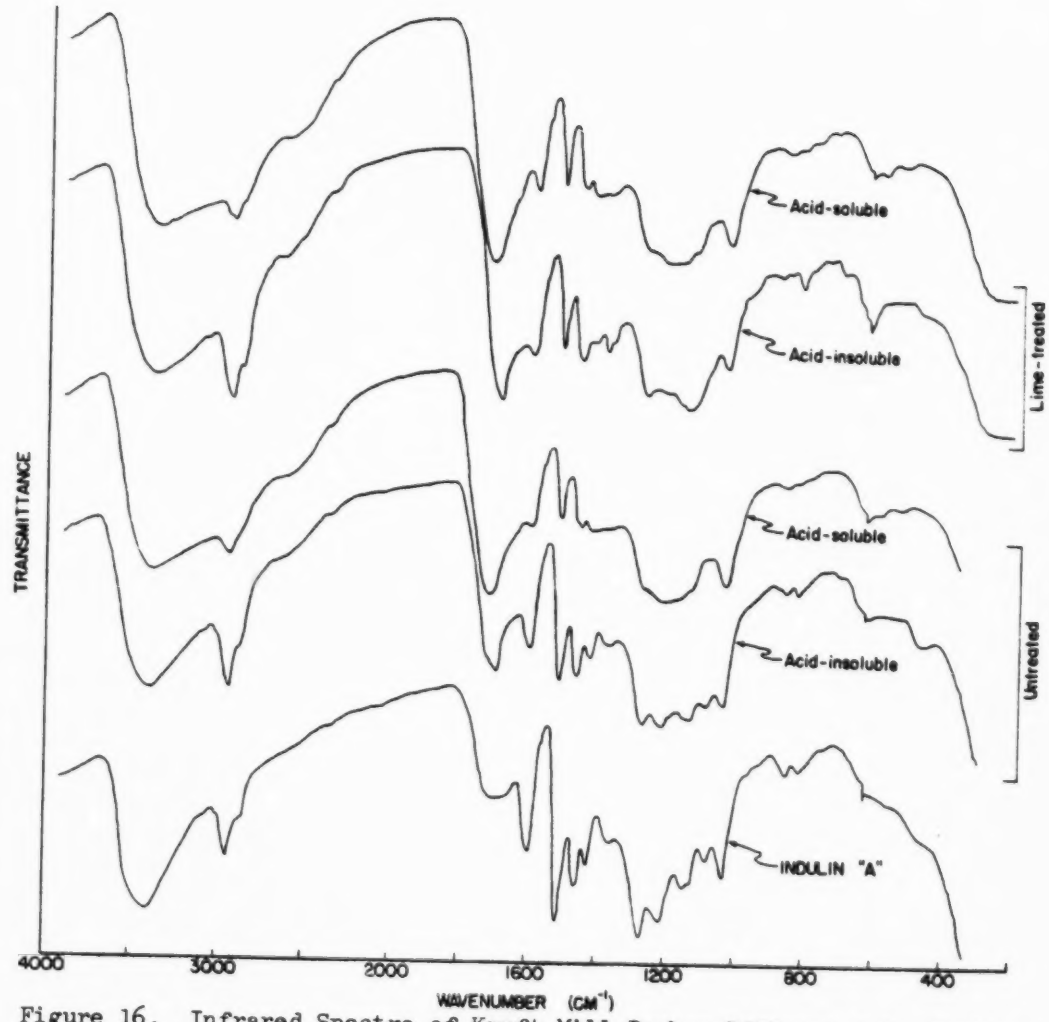

Figure 16. Infrared Spectra of Kraft Mill Decker Effluent Color Bodies

and all of the acid-soluble samples, and that is the greater breadth of absorption in the acid-soluble sample spectra in the 2500-3600 cm^{-1} region. These spectra all contain pronounced shoulders at about 2650 cm^{-1} which are characteristic of carboxylic acid dimers. Hence, it appears that carboxylic acid groups are more prevalent in the acid-soluble materials than in Indulin A.

2. C=O stretch (1680-1730 cm^{-1})

Indulin A shows a carbonyl absorption centered at about 1690, but it is quite broad (water contribution?) and is of medium intensity. All of the acid-soluble sample spectra show strong carbonyl absorption at approximately 1715 cm^{-1}. This may primarily reflect the greater abundance of carboxyl groups already suggested, but it would also be consistent with other types of carbonyl systems.

3. Aromatic ring vibrations (1450-1600 cm^{-1})

The three most important bands due to skeletal vibrations of the aromatic ring are those at about 1460, 1500, and 1600 cm^{-1}. The spectrum of Indulin A shows these bands at 1460 medium-strong intensity, 1510 strong, and 1595 medium. The spectra of the acid-soluble materials contain all of these bands although the relative intensities are somewhat different and they vary from sample to sample (the 1595 band is affected somewhat by the water absorption band which it partly overlaps).

4. The region 1000-1400 cm^{-1}

In this fingerprint region, the Indulin A spectrum shows five distinct absorption bands. The acid-soluble materials contain one of these at 1030 cm^{-1} (probably due to ether linkages), but the remainder of the region contains a very broad absorption band with several inflections. The broad character of this absorption can, in part, be due to the inorganic material present; sulfate salts give strong absorption in the region 1080-1130 cm^{-1}.

The intensity of the bands in this area is greater relative to the aromatic vibrations (1460-1600 cm^{-1}) that exist for the Indulin A spectrum. It is unlikely that sulfate absorption is the sole cause. Such a difference in intensities might be due partly to carbohydrate material present in the acid-soluble samples. However, such an inference demands additional support.

The spectrum of Indulin A contains an absorption <u>minimum</u> at 1400 cm^{-1}, but the acid-soluble sample spectra show

a broad absorption plateau at this frequency. This difference was also noted between the acid-soluble and acid-insoluble samples. The reason is not clear; carboxylic acid groups should contribute absorption to this region and may be partly responsible.

5. Out-of-plane C-H bonding (750-900 cm^{-1})

   The spectrum of Indulin A contains weak absorption bands at 812 and 850 cm^{-1}. This is comparable to what would be expected for a guaiacyl system (1,2,4-trisubstituted aromatic).

   Although they are weak bands, these absorption bands are still quite evident in the spectra of the acid-soluble samples. Hence, it would appear that orientation of groups on the aromatic rings is not markedly different from Indulin A.

Acid-Insoluble Samples (Untreated and Lime-Treated)

The spectra of untreated and lime-treated samples were similar but not identical. The differences were more substantial than was the case for the acid-soluble samples. These differences will be mentioned below in the appropriate sections.

1. OH and CH stretch (2500-3600 cm^{-1})

   The very broad absorption in this region previously mentioned for the acid-soluble samples was also found for the acid-insoluble samples. Here again the broad absorption contained a pronounced inflection at 2650 cm^{-1}. It thus appears that carboxylic acid groups are present in both the acid-soluble and acid-insoluble samples, and they are more prevalent in these samples than in Indulin A.

   The lime-treated and untreated samples (acid-insoluble) gave virtually the same spectra in this limited region.

   An interesting difference between the acid-soluble and acid-insoluble samples is revealed by the CH component of this absorption. The acid-insoluble materials show a much better resolved aliphatic CH absorption band at 2940 cm^{-1}. It is also a more important component (intensity) of this broad absorption envelope than is the case for the acid-soluble material.

2. C=O stretch (1680-1700 cm^{-1})

   The carbonyl band in these spectra was a strong absorption band at about 1695 cm^{-1}. Its position is essentially the

same in lime-treated and untreated samples. The absorption is considerably stronger and sharper than the band at 1690 cm^{-1} found in the spectrum of Indulin A.

The difference of approximately 20 cm^{-1} between the carbonyl bands of the acid-soluble and acid-insoluble samples is significant and appears to suggest some important differences in carbonyl groups. The 1695 band in the acid-insoluble samples could be a result of an appreciable quantity of conjugated carbonyl units. These carbonyls could be present as ketones, acids or both. A reasonable conclusion is that the acid-insoluble samples contain a greater amount of conjugated carbonyl groups than the acid-soluble samples.

3. Aromatic ring vibrations (1450-1600 cm^{-1})

The three characteristic bands for aromatic (including lignin) structures are again evident. The relative intensities of these bands differ somewhat from sample to sample. The ratio of absorbances for the bands at 1510 and 2900 were examined since the former is a relatively "pure" aromatic band and the latter is due to aliphatic methylene and methyl groups. The comparison revealed that the ratio A_{1510}/A_{2900} is lower in the acid-insoluble materials than in Indulin A. This result coupled with the preceding discussion of the CH absorption band at 2900 seems to suggest that, in comparison to Indulin A, the acid-soluble and acid-insoluble samples contain different proportions of aliphatic and aromatic structural groups.

4. The region 1000-1420 cm^{-1}

The broad absorption band (1100-1300 cm^{-1}) which is present in the acid-soluble samples is not duplicated in the acid-insoluble samples. The untreated samples gave spectra containing five peaks and resembling the Indulin A spectrum. Two of these peaks are not evident in the spectra of the lime-treated samples, but the higher percentage of inorganic material (11-17 percent ash) in these samples probably contributes to the strong absorption at 1140 cm^{-1} and could well mask other bands in that neighborhood.

Indulin A gave a peak at 1425 cm^{-1} which also appeared in the untreated acid-insoluble sample spectra. However, the lime-treated acid-insoluble samples showed only a shoulder at that frequency. The 1425 cm^{-1} band in lignin-containing-materials is generally assigned to C-H bonding in methoxyl groups; therefore, the intensity differences are probably due to a relatively low methoxyl content in

the lime-treated acid-insoluble samples. The experimental methoxyl contents in the samples correlate well with the relative intensity of the 1425 band in the sample spectra.

The minimum at 1400 cm^{-1} which is present in the Indulin A spectrum is also present in the acid-insoluble samples which contrasts with the acid-soluble samples. The acid-insoluble sample spectra contain an additional band at 1385 cm^{-1} which is not present in the Indulin A spectrum. In this respect, there seems to be little difference between the acid-soluble and acid-insoluble samples. The significance of the 1385 cm^{-1} band is not clear.

5. Out-of-plane C-H bonding (750-900 cm^{-1})

There is an interesting difference (relative to Indulin A) in this area with regard to the relative intensities of the 820 and 855 cm^{-1} bands. In Indulin A these bands are comparable in intensity, as is the case with the untreated sample, whereas the lime-treated acid-insoluble samples show a much more intense band at 820 than the ill-defined band at 855 cm^{-1}. This region characterizes the substitution pattern of aromatic rings so the difference observed might indicate a change in the substitution pattern (possibly due to condensation). However, the value of these bands as good group frequencies is markedly reduced if an electron-withdrawing group (such as a carbonyl group) is attached to the aromatic ring. Thus, the difference observed may be related to the observation discussed earlier concerning the presence of conjugated carbonyl groups. Perhaps these carbonyl groups are conjugated directly with the aromatic ring, and the relative intensities of the bands at 820 and 855 cm^{-1} are perturbed as a result of this conjugation.

The observations from the IR study are summarized as follows:

The acid-insoluble and acid-soluble components of both untreated and lime-treated samples, as well as Indulin A, gave absorption bands at 1460, 1500, and 1600 cm^{-1}, indicating the presence of aromatic structures.

Both acid-soluble and acid-insoluble samples show greater carboxylic acid absorption than does Indulin A. Indulin A gave a relatively weak carbonyl band at 1690 cm^{-1}, whereas the acid-insoluble fractions gave a strong band at about 1695 cm^{-1} and the acid-soluble fractions gave a strong band at approximately 1715 cm^{-1}. Different carbonyl stretching frequencies distinguish the acid-soluble from the acid-insoluble samples but lime treatment itself does not influence these frequencies. The acid-insoluble fractions seem to contain a high proportion of carbonyl

groups (carboxyl, ketone, or both) conjugated with an aromatic ring, whereas the acid-soluble fractions seem to contain nonconjugated carboxyl groups.

The intensities of bands (1425, 1450 cm^{-1}) normally associated with methoxyl groups correlate well with the experimental methoxyl contents. Comparison of bands (1500-1600, 2900-3100 cm^{-1}) related to aromatic and aliphatic structures suggest possibly marked differences between the acid-soluble and acid-insoluble materials.

The acid-insoluble samples show greater differences as a result of lime treatment, but these differences may be entirely due to differences in ash and methoxyl content. The acid-soluble samples reveal very few, if any, significant differences as a result of lime treatment.

The broad, intense absorption band near 1200 cm^{-1} in the spectra of acid-soluble materials may be due, in part, to associated carbohydrate material.

Molecular Weight Distribution

Molecular weights of some selected fractions of acid-insoluble and acid-soluble components of the untreated and lime-treated color bodies were determined by the sedimentation equilibrium method using the analytical ultracentrifuge[13]. The maximum and minimum values, in other words the molecular weight ranges, of the abovementioned color bodies, are plotted in Figures 17, 18, 19, and 20. The dotted area represents tne molecular weight ranges and also indicates the heterogeneity of each fraction. To simplify matters, the apparent "weight average" molecular weights (M_w) for each fraction were calculated from the range data and are plotted in Figures 21 and 22.

Figure 21 shows that M_w of untreated acid-insoluble components are much higher than that of the lime-treated acid-insoluble component. The M_w values drop sharply, level off, and then rise slightly near fractions "J" and "K." Theoretically, the gel chromatography should yield samples with regularly decreasing molecular weights. The reason for this shift in property of the gel was not pursued.

Acid-soluble color bodies, on the other hand, seem to behave differently (Figure 22). In this case, the A1 and A5 fractions of the lime-treated color bodies show higher M_w values than that of the untreated color bodies. It seems that some of the higher molecular weight material in the lime-treated color bodies did not precipitate out during the acid treatment, indicating a slightly different character. It should be noted here also that comparatively more color remained in solution when the lime-treated material was acidified (see also Table 9).

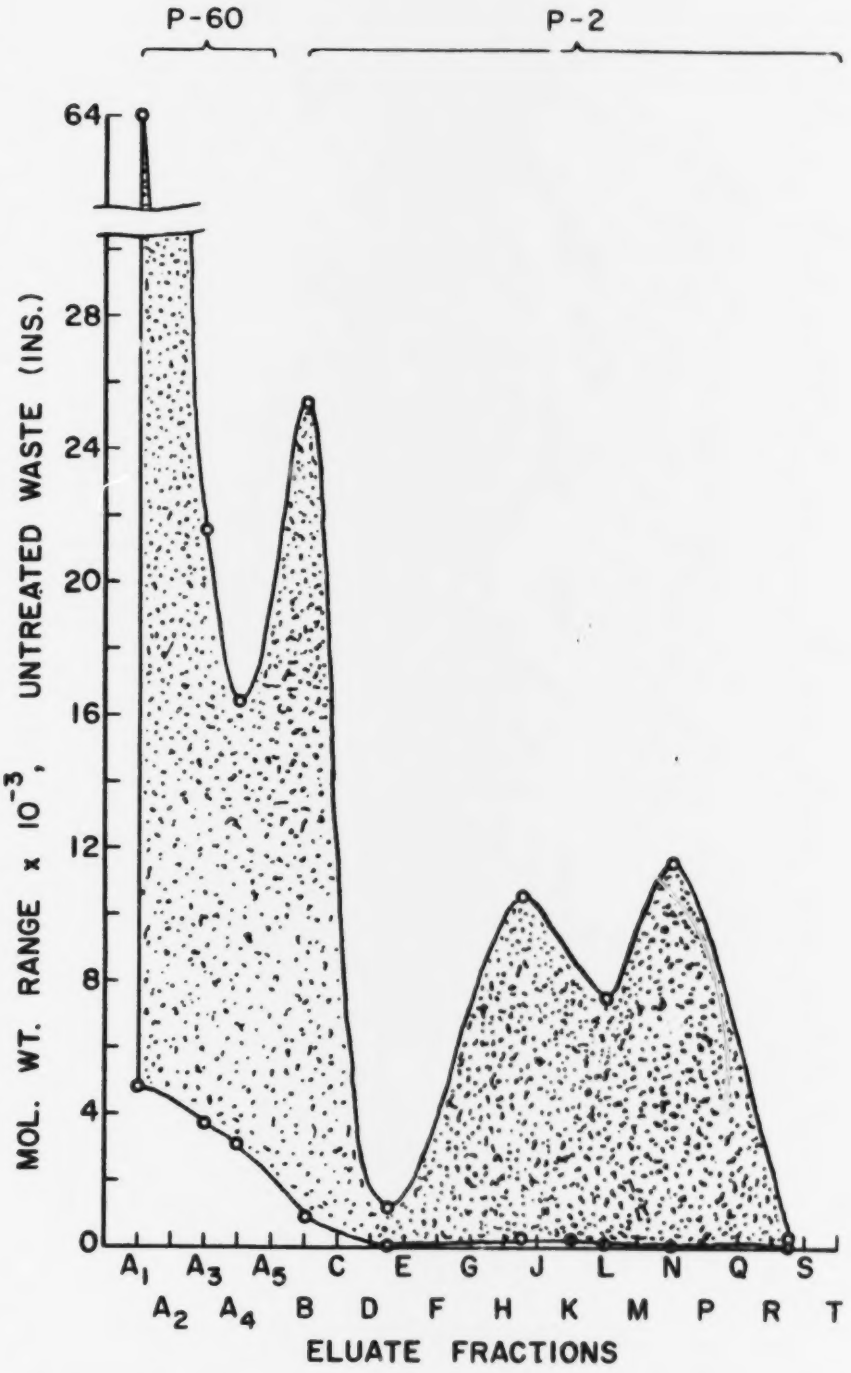

Figure 17. Molecular Weight Ranges and Distribution of Fractionated, Untreated Acid-Insoluble Color Bodies

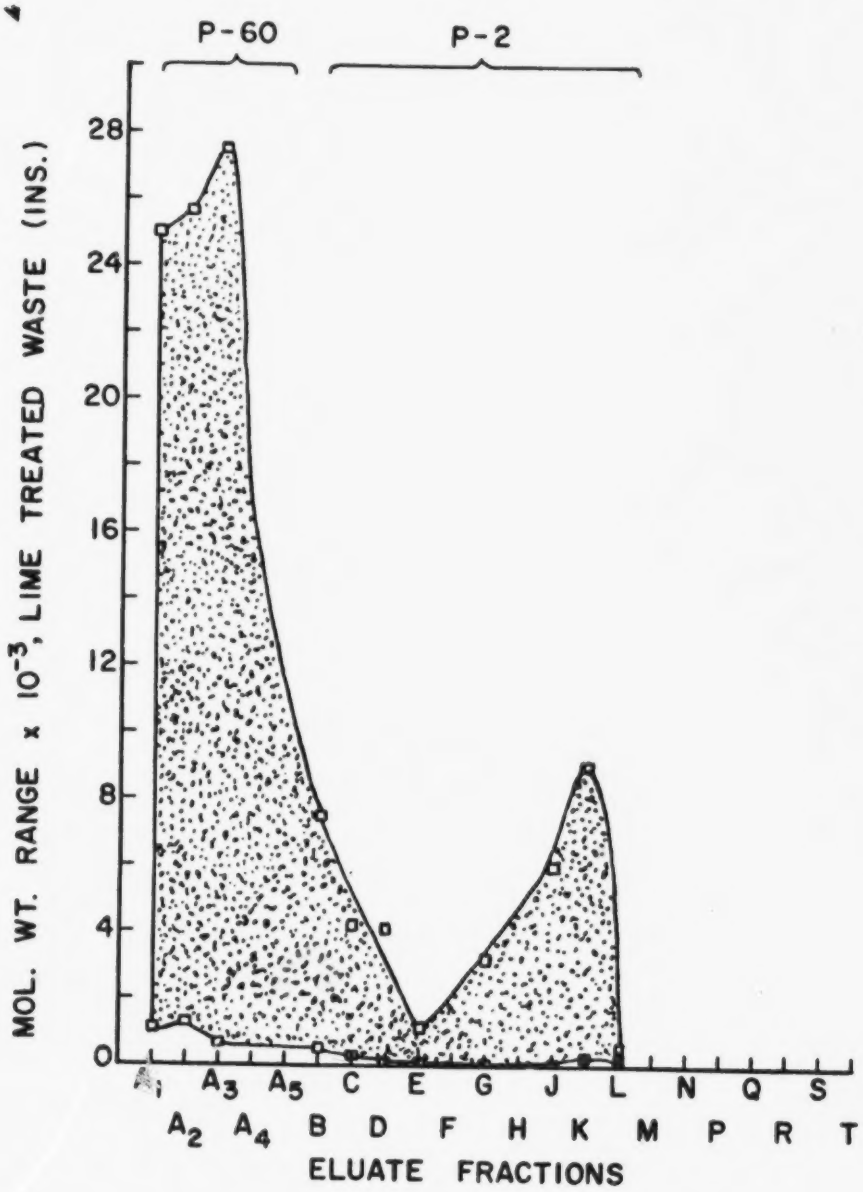

Figure 18. Molecular Weight Ranges and Distribution of Fractionated, Lime-Treated Acid-Insoluble Color Bodies

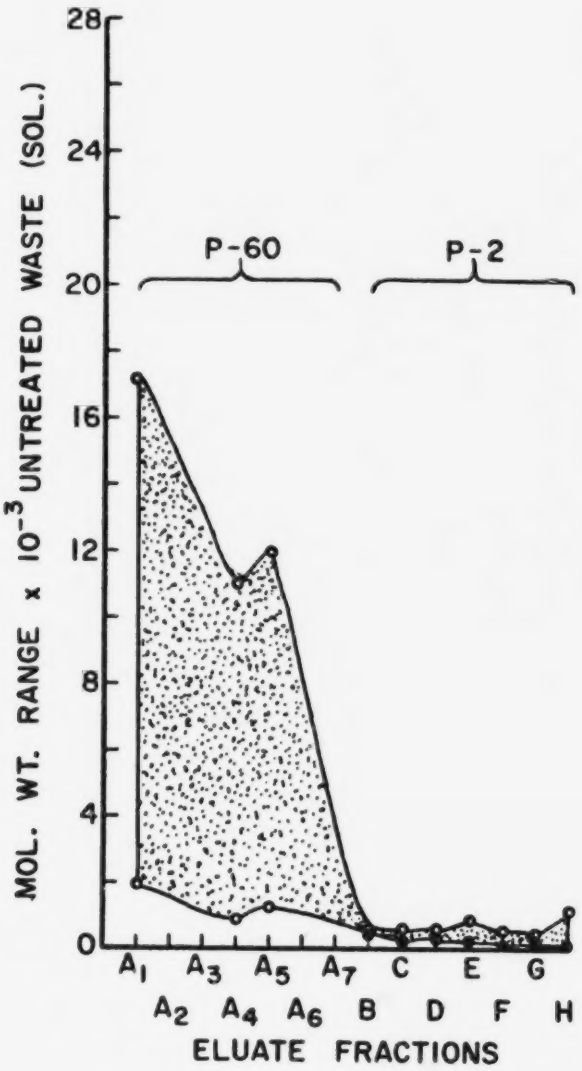

Figure 19. Molecular Weight Ranges and Distribution of Fractionated, Untreated Acid-Soluble Color Bodies

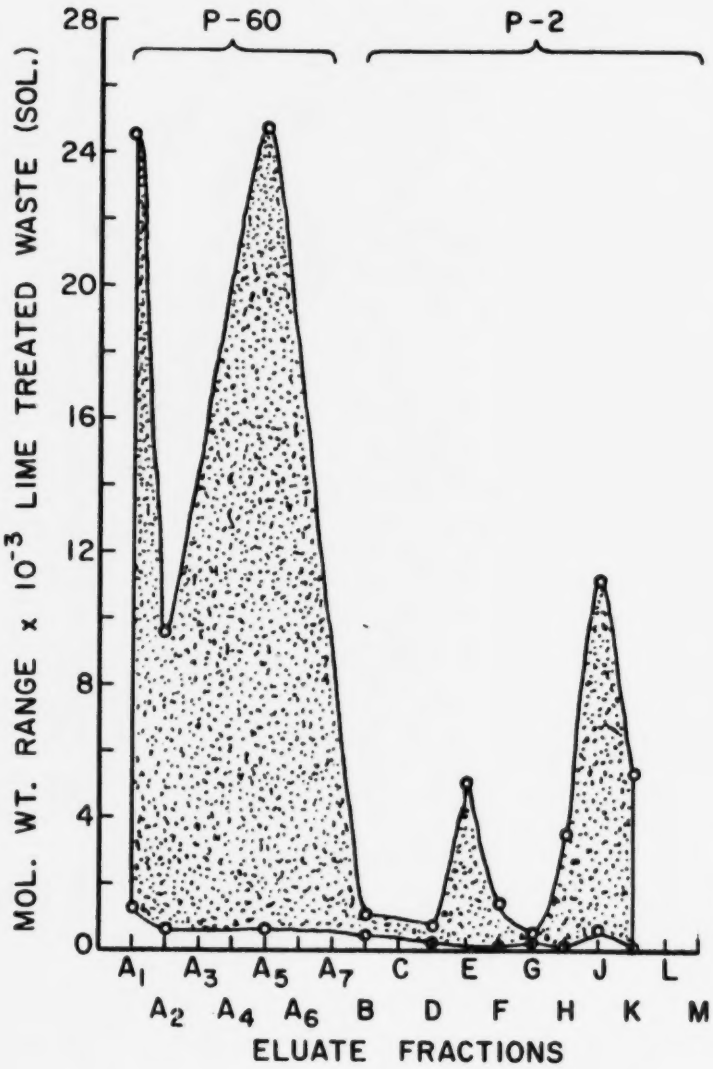

Figure 20. Molecular Weight Ranges and Distribution of Fractionated, Lime-Treated Acid-Soluble Color Bodies

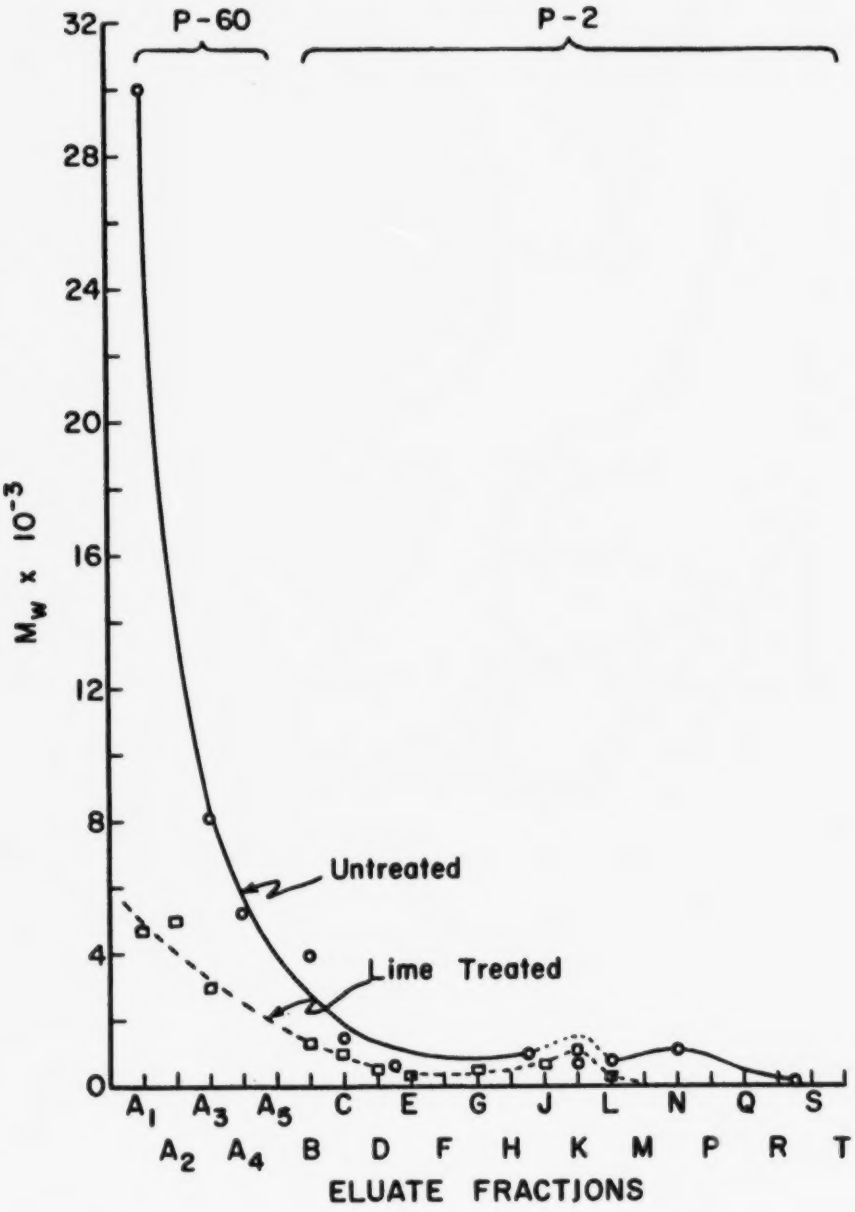

Figure 21. Weight Average Molecular Weight (M_w) Distribution of Fractionated Acid-Insoluble Color Bodies

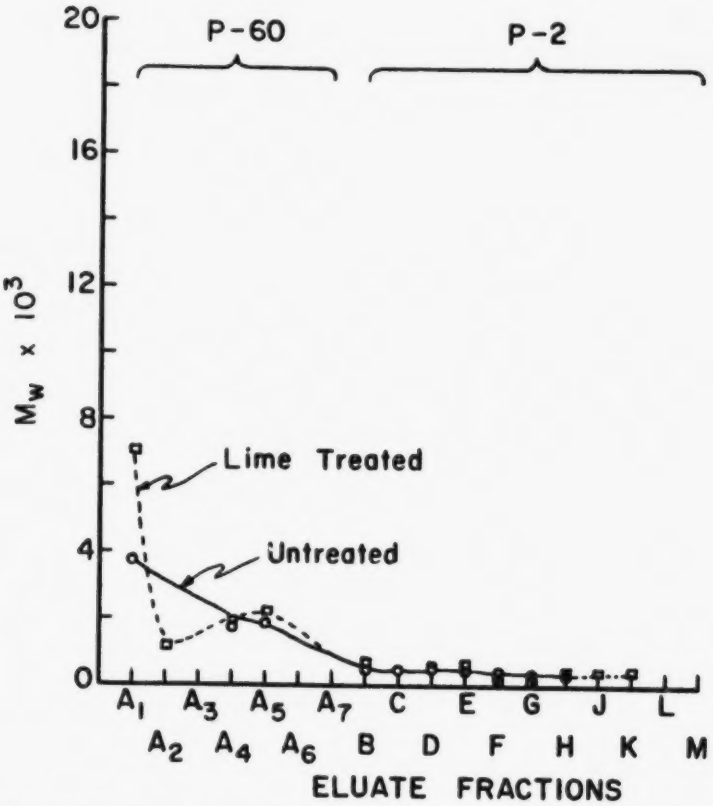

Figure 22. Weight Average Molecular Weight (M_w) Distribution of Fractionated Acid-Soluble Color Bodies

The percentage removal of color was calculated from the analytical data for both acid--insoluble and acid-soluble components and is plotted against their respective molecular "weight averages" in Figures 23 and 24.

Figure 23 shows that color bodies, in the acid-insoluble components, having a M_w of less than 400 are not removed by the lime treatment and those above M_w 5000 are completely removed. The intermediate range (M_w 400 to 5000) apparently undergoes partial removal. However, over 80 percent removal occurs above a M_w of 700 and 1000.

In the case of the acid-soluble component, percent removal levels off at 85 (Figure 24).

This suggests that any treatment which will increase the molecular size and weight of color bodies will favor complete removal.

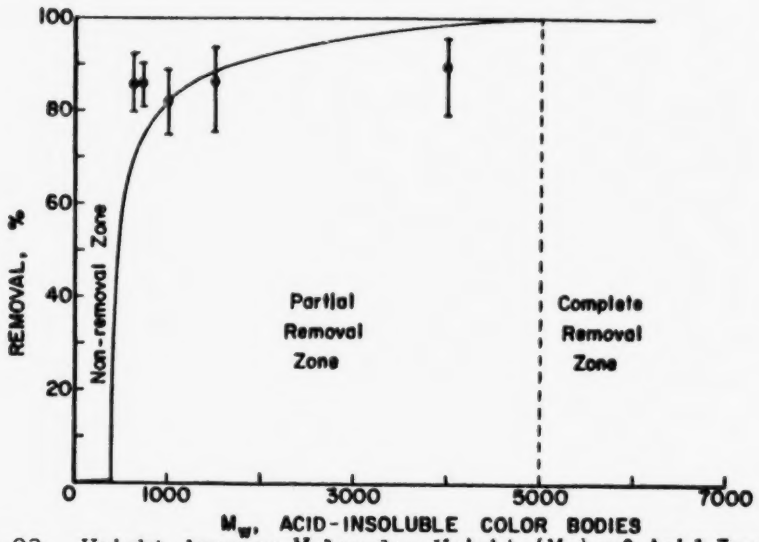

Figure 23. Weight Average Molecular Weight (M_w) of Acid-Insoluble Color Bodies Versus the Degree of Removal by Lime Treatment

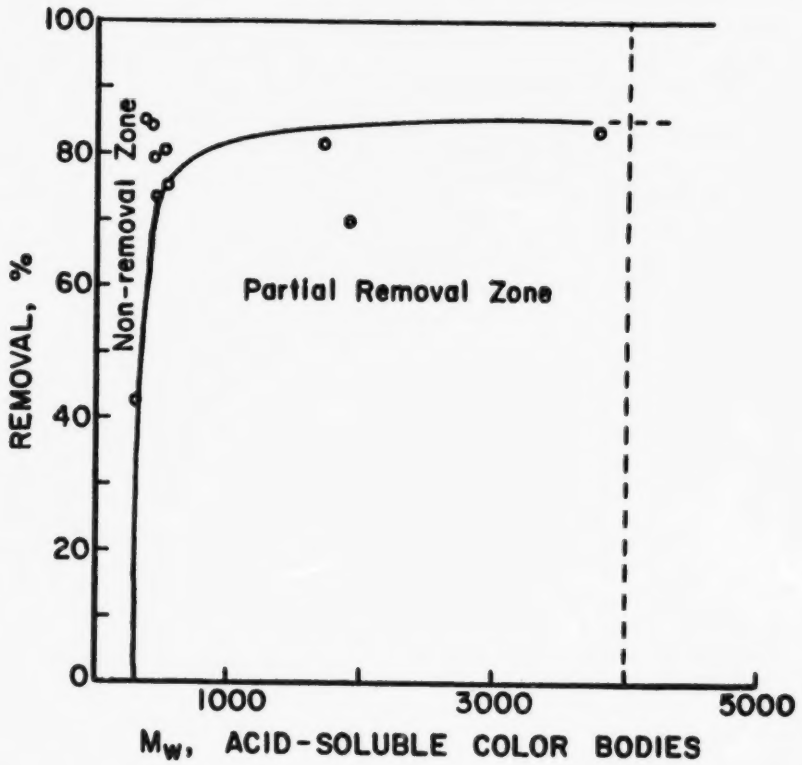

Figure 24. Weight Average Molecular Weight (M_w) of Acid-Soluble Color Bodies Versus the Degree of Removal by Lime Treatment

Electrokinetic Properties

Gel electrophoresis[14] was used to achieve migration of color bodies under an electric field. All color bodies migrated toward the anode, indicating that they were negatively charged.

Electrophoretic mobilities were calculated according to Ornstein[15] and relative mobilities were obtained by dividing these values by the Indulin C values. Results are given in Table 15.

Except for one untreated acid-insoluble fraction, and two lime-treated acid-soluble fractions, all color bodies showed higher mobilities than Indulin, indicating a higher density of negative charge per molecule. This suggests that the color bodies are more degraded than Indulin.

Pyrolysis Gas Chromatography of Color Bodies

In order to learn as much as possible from the small amounts of color bodies available, pyrolysis gas chromatography was carried out. A comparison of the complex chromatograms of selected color bodies to those obtained from a kraft liquor (Indulin C) qualitatively supported the other data which relate these fractions to kraft lignin. It might be expected that the more highly degraded smaller molecules found in the acid-soluble fractions would at least resemble lignin in chemical behavior. An inspection of Figure 25 indicates that the chromatograms of the several pyrolyzed fractions appear to be consistent with these hypotheses:

(1) the color bodies are degraded lignin fragments,
(2) the lower the solubility in acid and the higher the molecular weight the more nearly do the fractions resemble isolated kraft lignin.

Although such chromatograms are relatively complex, it may be possible to utilize the technique in future studies to elucidate further the chemical nature of such materials.

TABLE 15

RELATIVE MOBILITIES OF COLOR BODIES BY GEL ELECTROPHORESIS

Sample	Relative Mobility[a]	Charge on Color Bodies
Untreated acid-insoluble fractions		
A1-2	0.969	Negative
A4-5	1.051	"
B-C	1.010	"
D-K	1.092	"
L	1.054	"
M-T	1.033	"
Untreated acid-soluble fractions		
A1-3	1.030	"
A4	1.010	"
A5-6	1.071	"
B-J	1.071	"
Lime-treated acid-insoluble fractions		
A1-2	1.071	"
A3, B-M	1.071	"
Lime-treated acid-soluble fractions		
A1-7	1.010	"
B-F	1.054	"
G	1.033	"
H	0.989	"
J	0.989	"
K	1.033	"
L	1.076	"

[a]Mobility of color bodies divided by that of Indulin 'C.'

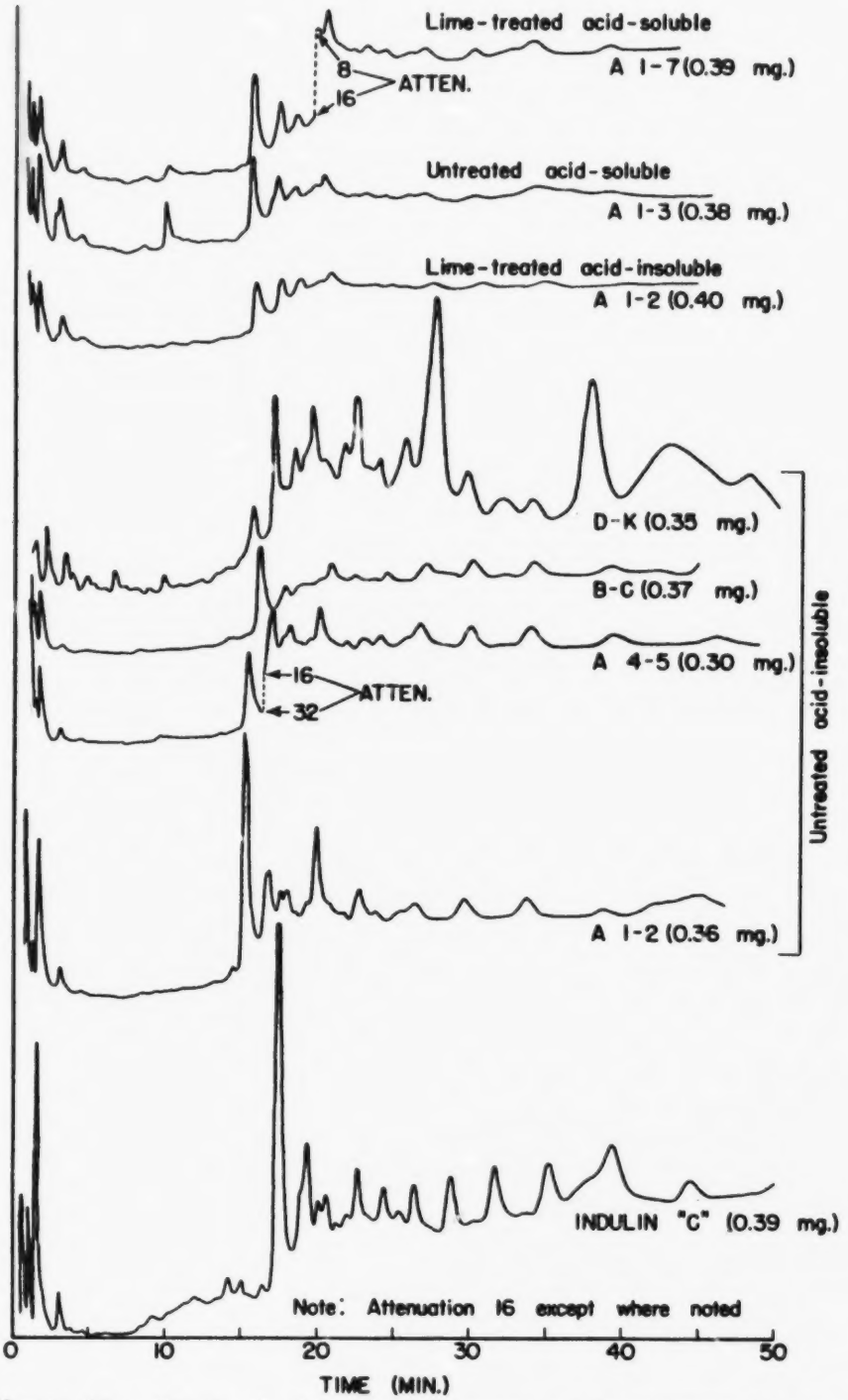

Figure 25. Pyrolysis Gas Chromatograms of Fractionated Color Bodies from the Kraft Mill Decker Effluents

SECTION VII

EXPERIMENTAL

Processing and Freeze-Drying of Wastes

Untreated and lime-treated colored samples were concentrated under reduced pressure to one-tenth of their original volume. (Untreated samples, if concentrated further, were very difficult to freeze-dry.) Most of the calcium, especially in the lime-treated samples, was precipitated by carbonating the samples to a pH of 10.2. The carbonated samples were then centrifuged in the Beta-centrifuge at 9000 rpm for 15 minutes. This speed and time was sufficient to give clear solutions. If, in some cases, slight turbidity was still present, these samples were filtered through a Millipore filter paper. The pH of the solution was checked at every stage. The colored but clear solutions were frozen in strong glass containers (centrifuge bottles) and dried under high vacuum. This freeze-dried material formed a low density powder and was readily soluble in water. The dried samples could be kept in airtight bottles for longer periods without any significant change.

Isolation of Acid-Insoluble Color Bodies from Freeze-Dried Solids

Freeze-dried solids of the untreated waste (14.3 g od basis) were dissolved under mechanical stirring in 60 ml of water and approximately 17 g of clean cellulose powder (Whatman standard grade) was suspended in the solution. The stirring was continued and the pH was adjusted to 1.0 with strong hydrochloric acid (1 vol concentrated acid to 2 vol of distilled water). The acidified mixture was filtered through a precoat of about 4 g of cellulose powder on a Buchner funnel and the filter cake was washed with a total of 50 ml of water in small portions. When the filtrate was just acid to Congo Red paper, some of the precipitate peptized and formed a cloudy filtrate. The cloudy filtrate was mixed with about 3 g of acid-washed Fibra-Flo 11C (Johns-Manville filter aid), the mixture was filtered on a thin precoat of Fibra-Flo on a small Buchner funnel, and the filter cake was washed with water.

Both the cellulose powder and the Fibra-Flo filter cakes were separately extracted with 50 percent aqueous ethanol. The alcohol was evaporated from the combined solution at reduced pressure whereupon a finely divided precipitate formed; the slurry containing this precipitate was subsequently freeze-dried, and designated as "acid-insolubles." The aqueous filtrate contained the "acid-soluble" material.

Isolation of Acid-Soluble Color Bodies

Both Amberlite MB3 and the combination Amberlite IR-120 followed by Amberlite IR-45 were tested for removal of the hydrochloric acid and other inorganics in the solution of acid-soluble color bodies. In both cases, large amounts of the color were retained by the resin.

All of the acid-soluble color was removed from the strongly acid solution with carbon (Draco), and there was some difficulty in filtering the carbon. Moreover, the sorbed color could not be removed completely from the carbon. Thus, neither ion exchange nor carbon seemed promising for separation of acid-soluble color bodies from the inorganic constituents. Finally, it was found that a large portion of the acid-soluble color bodies could be sorbed on Amberlite XAD-2 (Rohm & Haas Co.) and could be removed by eluting the resin with 50 percent ethanol. Most of the color was sorbed at the top of the column from the strong acid solution, but it moved slowly down the column as the excess acid was washed from the column. The acid passed through the column faster than the color, and most of the latter remained on the column when essentially all of the acid had been washed out. Additional color bodies were recovered by concentrating the aqueous solution and the washings which passed through the column, and then adding the concentrate to a smaller column of XAD-2. The sorbed color was readily removed by eluting the columns with 50 percent ethanol.

Paper Chromatography

Following preliminary experiments, 0.202 g of untreated freeze-dried color bodies was dissolved in 3.2 ml water and the solution was applied as evenly as possible to 8 strips of Whatman 3MM filter paper (23 cm x 28 cm). Thus, each strip carried approximately 0.0252 g of material. The strips were air dried overnight and were developed in an apparatus for descending chromatography. Chromatograms were developed in a mixed solvent designated herein as BWA, butane — water — acetic acid, 100:33:15. In about 2 hours the solvent had traveled 19 cm from the starting line. There was considerable streaking, but four more-or-less distinct brown-colored bands were present with additional brown-colored material at the solvent front and at the starting line. The papers were dried and were sectioned into seven bands or zones for subsequent elution.

The corresponding zones from 6 to the 8 original strips, equivalent to 0.152 g of the total, 0.202 g, were eluted with 50 percent aqueous ethyl alcohol.

The above procedure was repeated with an untreated sample which had been treated with an ion exchange resin, Amberlite IR-120, to remove the

cations. The chromatograms streaked or channeled badly, and no further work was done with this method of separation.

Color Measurement

Color was measured according to the platinum cobalt standard method of the American Public Health Association (APHA)[9]. The only modification of the method was the use of a noncarbonate buffer for pH adjustment to 7.6. It was necessary to have color values at a constant pH of 7.6, because color was found to be pH dependent. Most natural waters have a pH range close to 7.6.

It should be noted that the color unit is a measure of color intensity. When it has been necessary to refer to the total amount of colored material in a solution this has been called "total color" and is the product of the color units and the volume of the solution.

Absorbance Measurement

The samples used for color measurement were also used for absorbance measurement at desired wavelengths on the Beckman DU Spectrophotometer. The values obtained were multiplied by the dilution factor to give absorbance of the concentrated solutions. Absorptivity was calculated by dividing the absorbance values by concentration in grams per liter.

Determination of Solids

Total solids were determined by evaporation of a measured volume of waste at 105°C overnight. The resultant weight of solids was expressed in milligrams per liter (mg/l) of waste.

Fixed and volatile solids were determined by igniting the total solids at 600°C in an electric muffle furnace to constant weight, usually requiring one hour. The loss on ignition is reported as mg/l volatile and the residue as mg/l fixed solids.

Total Organic Carbon (TOC)

The Process Carbonaceous Analyser (Beckman & Co.) was used for this purpose. Because this instrument gives only total carbon values, TOC was determined by a modified direct method. The matters were further complicated by very small quantities of the fractions. To conserve color bodies, the majority of the specimens tested for TOC had been examined

for color which necessitated dilution within the color range of the platinum cobalt reference Nessler tubes.

For manual injections into the carbonaceous analyzer, an aliquot was prepared as follows:

> A 5-ml aliquot was transferred to a 30-ml glass beaker for a 5-ml volumetric flask. The pH of the specimen was adjusted to 2.9 to 3.0 with a 0.1N HCl solution (normally two milliliters were necessary). The acidified sample was rinsed with distilled water into a 2.5 x 15 cm test tube, having a 2-ml graduation mark, and the volume was reduced to 2.0 ml by boiling over a gas flame. The boiled sample was then transferred back to the 5-ml volumetric flask and the test tube was rinsed with 3 ml of pH 10 buffer (borax and sodium hydroxide) and added to the volumetric flask to give a combined 5-ml pH 10.0 specimen. Prior to injection into the carbon analyzer, the specimens were cooled to room temperature under the cold water tap. Volume was checked after cooling and adjusted to 5 ml if necessary.
>
> Twenty-three microliters of the specimens were injected at 3 to 5-minute intervals and an average reading was thus obtained from which the "blank" reading was subtracted to give the TOC value in mg/l.
>
> The "blank" consisted of all the ingredients listed above minus the sample and was handled in the same manner as the sample.

The analyzer was operated at 950°C according to instructions in the instrument manual. In addition to the precautions listed in the operating manual, the following precautions are recommended for accurate results.

a. The injection syringe should be checked often for burrs, cracks, etc., which cause particles from the rubber cap to drop into the combustion tube thus giving high readings.

b. A constant slow needle insertion and retraction is essential to prevent "popping" of the combustion chamber rubber cap.

c. Combustion chamber rubber cap should be replaced often.

d. Tygon tubing close to the condenser, filters, and glass combustion chamber dome should be cleaned often.

Fractionation of Color Bodies

Two types of Bio-Gels (Bio Rad Co.) were used for this purpose. Bio-Gel P-2 (exclusion limit 2600) and P-60 (exclusion limit 60,000) were hydrated in distilled water and separately packed in 2.5 x 200 cm and 2.5 x 100 cm glass columns, respectively. The complete apparatus used for fractionation is shown in Figure 26.

The volume of the solutions used for fractionation was less than 3 percent of the void volume of the column (void volume, Vo, = total bed volume x 0.38). A measured quantity of the solution was added to the top of the column. A glass fiber filter was used on the gel so that upon addition of the solution, the gel surface is not disturbed. The eluate was allowed to flow into an automatic collecting device and the collector timer and the UV-cord recorder were started. When the solution dropped to just below the surface of the gel, one milliliter of distilled water was added to the column and elution continued. When the level was again slightly below the gel, more distilled water was added and the column was then connected to the constant head water reservoir through a filter and a flowmeter. The elution rate (0.2-0.3 ml/min) was controlled by a teflon stopcock with a needle adjust. Fractions were collected every 30 minutes. At the end of fractionation, which took three to four days, the collected fractions were combined according to the number of peaks on the UV recorded chart. The combined fractions were freeze-dried and used for study. (Aliquots of the fractions were taken for color, TOC, and absorbance before freeze drying.)

Determination of Molecular Weights

Molecular weights were measured by the sedimentation equilibrium method[13]. In this procedure the centrifuge is run at an appropriate motor speed for a period of time necessary to achieve an equilibrium condition (rate of transport in one direction due to sedimentation balanced by the rate of transport due to diffusion in the other direction). Having achieved this condition, the technique requires the accurate measurement of the solute concentration distribution throughout the cell. The equilibrium condition is a practical one in which the concentration distribution does not change with time within the measuring experimental errors. Interference optics provides an accurate photographic record of concentration change from one position in the cell to another. A separate synthetic boundary run determines the initial concentration in terms of a total interference fringe shift.

Other data needed to compute molecular weights are rotor speed, temperature, partial specific volume of the solute, and density of the solution.

The densities of the solutions were measured according to the method described by Bauer[16] and plotted against their respective concentrations

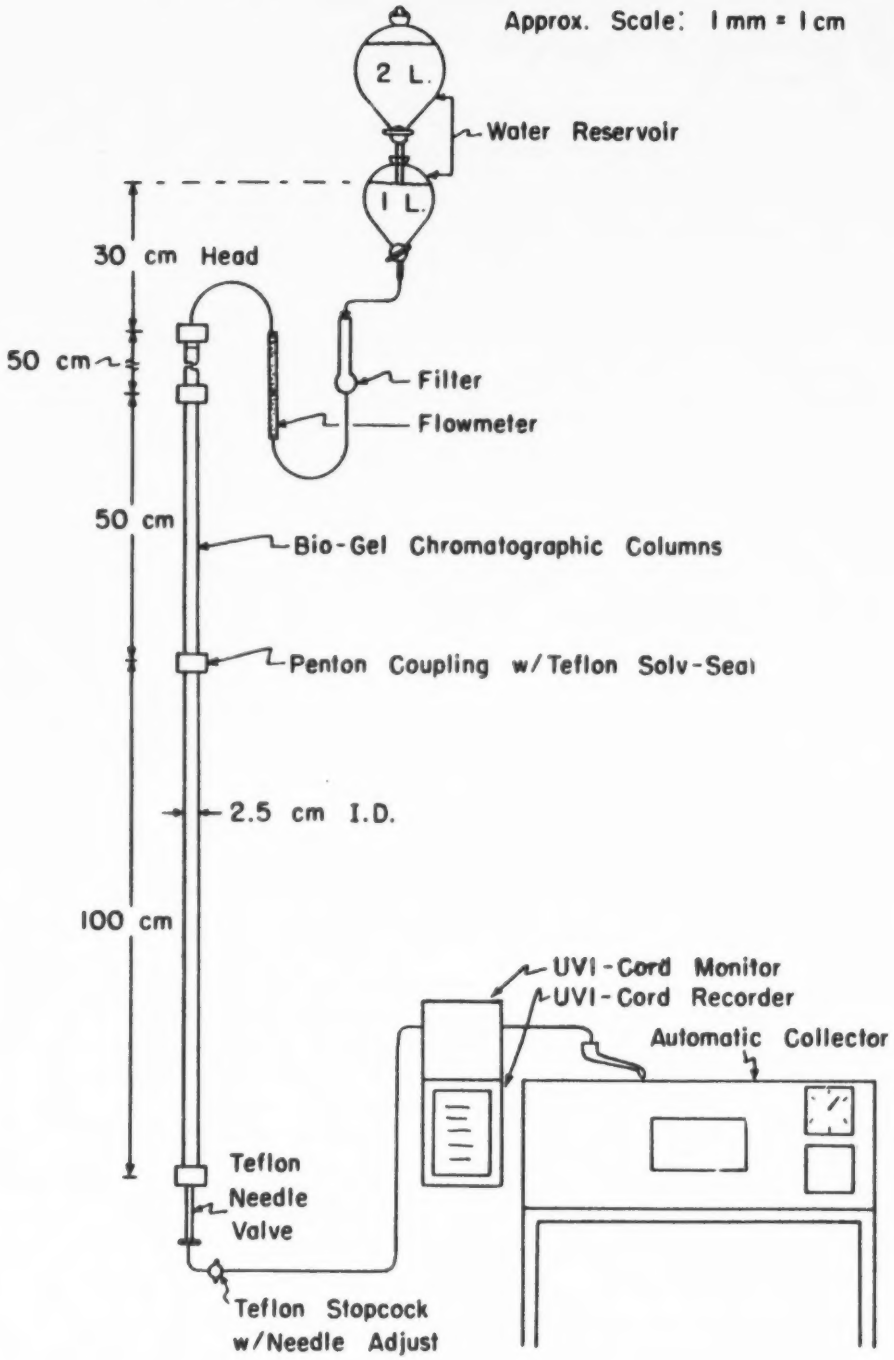

Figure 26. Diagram of Gel Permeation Chromatography Apparatus

in g/ml. A straight-line plot was developed and the partial specific volume, $\bar{V}$, was calculated from the straight-line relationship using Equation (1).

$$\bar{V} = \frac{1}{do} - \left[\left(\frac{1}{x}\right)\left(\frac{d - do}{do}\right)\right] \qquad (1)$$

where

x = concentration, g/ml
do = density of solvent
d = density of solution

A computer program (MOLWT) [a modification of the program by Teller[17]] was used for calculating the weight average molecular weights.

Disk Electrophoresis

The techniques and apparatus used were as described by Davis[14] with slight modifications.

The apparatus consisted of two Plexiglas (3/8-inch) buffer vessels (16.5 cm diameter and 9.0 cm deep) each with a centrally located electrode. The bottom of the upper vessel had 12 equally spaced holes along a bottom circumference. Bored out serum stoppers in these holes accept 5 x 100 mm glass tubes (gel columns). This buffer vessel was supported above the other so that the lower ends of the gel columns extended about 1/4 inch below the surface of the buffer in the lower vessel. Any bubbles formed on the gel column ends were removed. The power supply was a RECO Model E 800-2, 750 volts, 200 ma maximum output.

Glass tubes (5 x 100 mm) were mounted with rubber caps in a rack and 1.4-ml small pore gel (separation gel) solution added to each followed by a water layer to insure a flat gel surface. After polymerization (30 minutes) the water was removed and the gel surface was washed with large pore spacer or stacking gel. Spacer gel (0.1 ml) was added, overlayed with water and photopolymerized for 30-45 minutes. After removal of the water layer, 0.1-ml colored sample (0.5 mg in 40 percent sucrose) was added. Buffer was then layered carefully to fill the tubes completely. The tubes were mounted in the grommets of the upper vessel, buffer was then added to the vessels and electrophoresis started. Length of the small pore separation gel was 7.2 cm.

Two preliminary runs were made. Untreated acid-insoluble sample Fraction A 1-2 was run at 0.0625, 0.125, 0.25, 0.5, 1.0, and 2.0 mg per tube. This sample was also run at 0.5 mg per tube with gel concentrations of 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 percent. At the higher monomer concentrations there was a general "smear" of material trailing the main single band; however, no other discrete bands were visible. In subsequent runs, based on these results, a "normal" 7.5 percent gel was used

with 0.5 mg sample per tube. Also, all samples were run at 400 volts, 34 ma for 60 minutes at room temperature. Following electrophoresis, the distance from the top of the separation gel in the middle of the colored band was measured and electrophoretic mobilities were calculated according to Ornstein[15].

Pyrolysis-Gas Chromatography

Selected samples of color bodies from dilute waste liquor were subjected to pyrolysis-gas chromatography. The conditions were as follows:

Column: 20 percent Carbowax; 5 ft x 1/8 inch
Initial temp 75°; final temp 225°
Rate 10°/min
Detector: Hydrogen flame ionization
Temp 265°
Injector: Temp 225°
Carrier gas: Helium at 30 ml/min
Pyrolysis: 9.5 amp for 12 sec to produce a maximum temp of 650°.

Sample	Amount Hydrolyzed, mg
Indulin C	0.39
Untreated acid-insoluble fraction	
A 1-2	0.36
A 4-5	0.30
B-C	0.37
D-K	0.35
Lime-treated acid-insoluble fraction	
A 1-2	0.40
Untreated acid-soluble fraction	
A 1-3	0.38
Lime-treated acid-soluble fraction	
A 1-7	0.39

Particles of suitable size and density for proper loading of the pyrolysis apparatus were prepared from the fluffy freeze-dried solids. A small droplet of water was placed on a microscope slide, the fluffy solid was carefully added to the droplet until a heavy paste was formed. The paste was dried in the air to a brittle solid from which suitable pieces were selected for the pyrolysis-GLC. The chromatograms are shown in Figure 25.

SECTION VIII

ACKNOWLEDGMENTS

The support of the President of The Institute of Paper Chemistry, Mr. John G. Strange, is acknowledged with sincere thanks. Mr. John W. Swanson, Director of the Division of Natural Materials and Systems of the Institute, was Project Director. Dr. Hardev S. Dugal, Research Associate of the Institute, was Project Leader and carried out much of the work himself and coordinated the work of others on this project. Dr. Marion A. Buchanan and Mr. Edgar Dickey were responsible for certain phases of isolation and characterization work. Portions of the experimental work were conducted by Messrs. Norman Colson, John Carlson, and Lowell Sell each of whom contributed to the work in the area of his specialty. Dr. Robert M. Leekley, Dr. Donald C. Johnson, and Mr. Carl Piper contributed through valuable suggestions and consultation.

Mr. Charles L. Davis, Jr., Pollution Control Director of Interstate Paper Corporation, and his staff periodically collected the samples of colored waste which were studied and contributed useful information about their lime treatment process.

The support of the project by the Office of Research and Monitoring, Environmental Protection Agency, and the help provided by Mr. Edmond P. Lomasney, Dr. James D. Gallup, and Mr. George R. Webster, the Grant Project Officer, is acknowledged with sincere thanks.

SECTION IX

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SECTION X

PUBLICATIONS

1. Dugal, Hardev S., Swanson, John W., Buchanan, Marion A., and Dickey, Edgar E. Chemical and Physical Nature of Color Bodies in Kraft Mill Effluents Before and After Lime Treatment. AIChE Sixty-fourth annual meeting, San Francisco, California, Nov. 28-Dec. 2, 1971, Paper 16C.

This paper was presented by Dr. H. S. Dugal at the AIChE 64th annual conference in San Francisco.

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SECTION XI

APPENDICES

I. Fractionation of color bodies: material balance based on color and TOC.

II. Detailed sugar analysis of untreated and lime-treated wastes.

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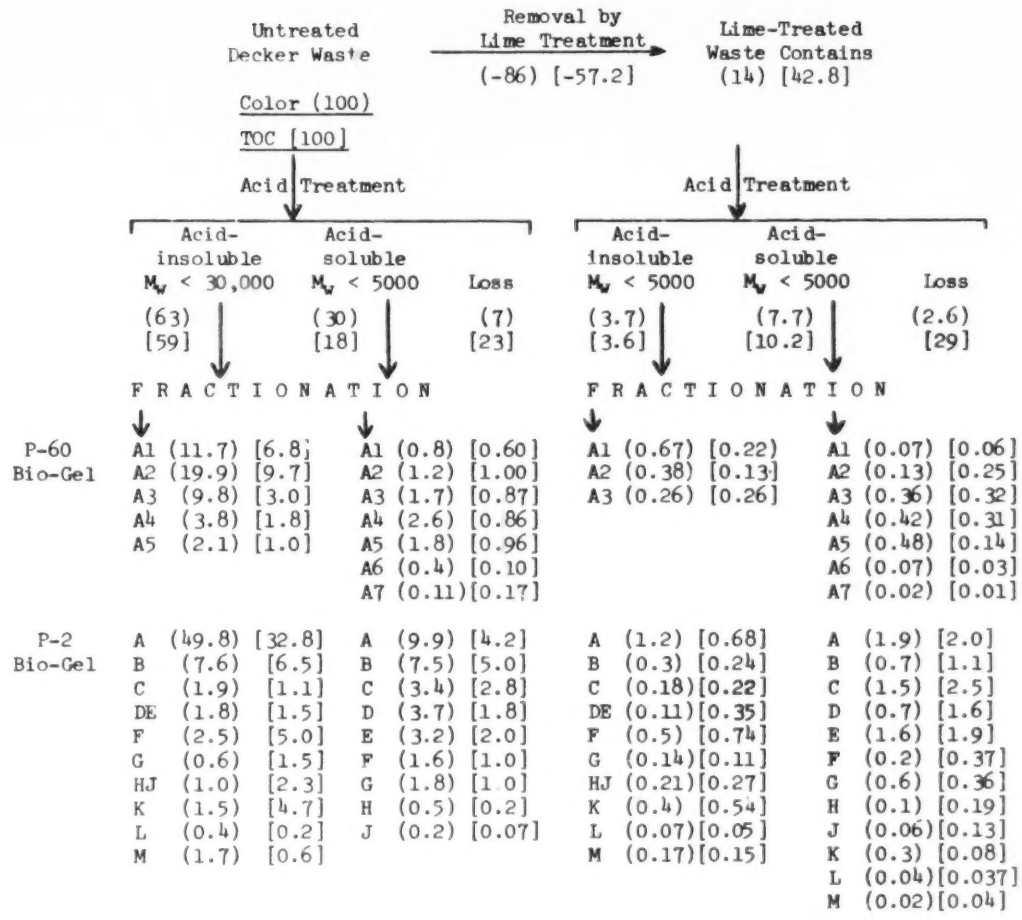
APPENDIX I

FRACTIONATION OF COLOR BODIES
(Material balance based on color and TOC)



All values calculated on the basis of untreated Decker waste taken as 100.
Color values are shown in parentheses and TOC in brackets.
Color bodies were first fractionated on Bio-Gel P-2 to give Fraction A-M.
Fraction 'A' from P-2 was further fractionated on Bio-Gel P-60 to give Fractions A1-A7.
M_w = weight average molecular weights.

APPENDIX II

DETAILED SUGAR ANALYSIS OF UNTREATED AND LIME-TREATED WASTES

Sample Fractions	Sugars[a], %						
	Rhamnan	Araban	Xylan	Mannan	Galactan	Glucan	Total
Untreated Waste	0.11	0.16	0.29	0.13	0.16	0.065	1.51
Acid-insoluble	0.018	0.31	0.13	0.19	0.12	0.41	1.60
Fraction A1-2	--	0.68	0.39	--	0.10	0.95	2.12
A3	--	0.22	0.43	--	0.03	0.26	0.94
A4-5	0.13	--	0.28	--	--	0.26	0.67
B-C	0.026	0.04	0.17	0.10	--	0.089	0.42
D-K	--	--	0.035	--	--	0.16	0.20
M-T	--	--	--	0.11	0.007	0.14	0.26
Acid-soluble	0.077	0.28	0.38	0.47	0.41	0.41	2.69
Fraction A1-3	0.047	0.35	3.0	--	--	0.84	4.24
A4	0.040	0.40	0.5	--	0.057	0.28	1.28
A5-6	0.40	0.30	1.2	--	--	4.20	6.10
B-J	--	0.59	0.78	--	0.27	0.081	1.72
Lime-Treated	0.15	0.13	0.80	0.27	0.074	0.008	2.92
Acid-insoluble	--	--	0.09	2.30	--	--	2.39
Fraction A1-2	--	0.37	0.81	--	--	1.7	2.88
A3, B-M	--	0.058	0.063	--	--	0.061	0.18
Acid-soluble	0.014	0.32	1.18	0.48	0.40	0.14	2.86
Fraction A1-7	--	0.94	3.1	0.20	0.65	1.0	5.89
B-F	--	0.54	0.96	--	0.18	0.2	1.88
Indulin 'C'	--	0.15	0.21	--	0.7	0.008	1.07

[a]Based on respective o.d. solids.

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